CHARACTERIZATION OF THIOPHENE-BASED CONDUCTING POLYMERS BY PYROLYSIS-GAS CHROMATOGRAPHY-MASS SPECTROMETRY

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Characterization of Thiophene-Based Conducting Polymers by Pyrolysis-Gas Chromatography-Mass Spectrometry

by

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Abstract

Conducting polymers have attracted great attention since their discovery at the end of the 70's due to their high conductivity, versatility and structural flexibility. Various methods have been developed for their structural characterization but few are useful for microstructure elucidation. This study demonstrates the ability of Pyrolysis-Gas Chromatography-Mass Spectrometry to examine both the thermal degradation behavior and microstructure of thiophene-based conducting polymers.

Unsubstituted polythiophenes, i.e., polythiophene, poly(2,2'-bithiophene), and poly(2,2':5',2"-terthiophene) were prepared by galvanostatical electropolymerization. β-substituted polythiophenes, i.e. poly (3-alkylthiophene)s (alkyl = methyl, hexyl, octyl), poly(3-methoxythiophene) and poly (3,4-ethylenedioxy-thiophene), were synthesized either electrochemically or chemically. Optimum pyrolysis temperatures for high yields of structurally-important fragments were established by investigating pyrolysis temperatures from 300 to 1400^{0}C. Comparison of polythiophenes shows that the yield of H_2S decreases, while the yield of thiophene oligomer fragments increases, as the chain length of the precursor oligomer increases. These results reflect decreasing the conjugation length from polythiophene to polyterthiophene. The predominant polymeric linkage in unsubstituted polythiophenes is α-α′ along with non-negligible amounts of α-β′ linkage. Evidence of partial overoxidation of polythiophene during electropolymerization was also obtained from the pyrograms. Structural analysis of oligomer fragments obtained from pyrolysis of poly(3-alkylthiophene)s gave useful stereoregularity information (i.e., head / tail configurations). Furthermore, based on the pyrolysis products, possible degradation pathways of poly(3-alkylthiophene)s were established.

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Dedication

To my husband Huan Huang and my parents, Wangshi Tang and Dichen Zhou, and my son Da Da

Abbreviations

BT	2,2'-bithiophene
CV	Cyclic Voltammetry
E_{pa}	Anodic Peak Potential
Et_4NBF_4	Tetraethylammonium Tetrafluroborate
FID	Flame Ionization Detector
GC	Gas Chromatography
GPC	Gel Permeation Chromatography
H	Head
IR	Infrared
MOT	3-methoxythiophene
MT	Monomethyl-thiophene
MBT	Monomethyl-bithiophene
METT	Monomethyl-tetrathiophene
MTT	Monomethyl-terthiophene
MS	Mass Spectrometry
NMR	Nuclear Magnetic Resonance Spectroscopy
PAT	Poly(3-alkylthiophene)
PBT	Poly(2,2'-bithiophene)
PEDOT	Poly(3,4-ethylenedioxythiophene)
PMT	Poly(3-methylthiophene)
PMOT	Poly(3-methoxythiophene)
PT	Polythiophene
PTT	Poly(2,2':5',2"-terthiophene)
PWHH	Peak Width at Half Height
Py	Analytical Pyrolysis
RSD	Relative Standard Deviation

SIM	Selected Ion Monitoring
TETT	2,2':5',2":5",2"'- quaterthiophene
TIC	Total Ion Chromatogram
T	Tail
Th	Thiophene
TT	2,2':5',2"- terthiophene
T_{py}	Pyrolysis Temperature
UV-Vis	Ultraviolet-Visible

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Chapter 1

Introduction

1.1 Background of Conducting Polymers

In a traditional view, organic and polymeric materials generally have poor electrical conductivities compared with metals and semiconductors. However, polymers have their own unique properties such as plasticity, toughness, high mechanical strength, corrosion resistance and light weight. With these properties polymers are used as a replacement for metals in many cases. In 1974, in an unexpected and encouraging experiment [1], Japanese chemist Shirakawa accidently prepared a silvery film of polyacetylene by mistaken addition of excess catalyst. This opened up the possibility of the preparation of conducting polymers. Later, in 1977, MacDiarmid's discovery of treatment of polyacetylene with Lewis acids or bases, increasing its conductivity by up to 13 orders of magnitude [2], marked the birth of the first conducting polymer.

Conducting polymers exhibit interesting electrical and electrochemical properties associated with their extended π-bonding system. Their electrical conductivity can be increased through appropriate chemical or electrochemical oxidation (p-type doping) or

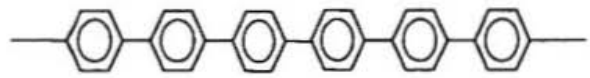
reduction (n-type doping). Based on their properties, conducting polymers have found potential applications in a wild range of fields including batteries [3,4], electronic displays [5,6], antistatic coatings [7], electrocatalysts [8], sensor technology [9], separation membranes and molecular electronics [10].

Besides polyacetylene, other conjugated polymers (Figure 1.1), including poly(phenylene), poly(pyrrole), poly(thiophene), and poly(aniline) have also been developed. Compared with the original polymer, polyacetylene, polymers containing heterocylic units have notable electrical conductivities, increased stability and processability in both the doped and neutral states. Among these polyheterocylics, polythiophene (PT) and its derivatives have sparked great interest because they exhibit a range of advantages [11,12]. They include applications of both the doped and neutral states, the reversibility of the transition between the doped and neutral states, their high conductivity, their redox activity and their potential for modification of their electric and electrochemical properties by manipulation of the monomer structure. This thesis will focus on thiophene-based conducting polymers.

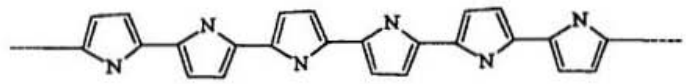
Conducting polymers are conductive due to their ability to carry an electric current under an applied voltage. However, differences in electronic structure determine how electrical conductivity varies from one polymer to another.

Poly(acetylene)

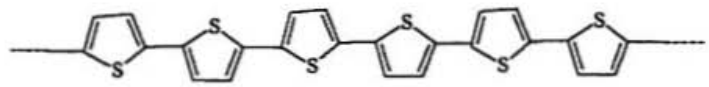
Poly(phenylene)



Poly(pyrrole)



Poly(thiophene)



Poly(aniline)

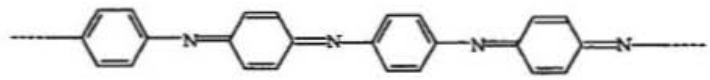


Figure 1.1 Examples of conjugated polymers

The band theory for solid state materials is widely accepted and applied for the explanation of the electronic structures of conducting polymers [13]. Figure 1.2 is the schematic band structure diagram. When monomers are polymerized into a polymer, the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) form two separate energy bands, the valence and conduction bands. The energy difference between the two bands is termed the band-gap. In the neutral form the valence band is filled, the conduction band is empty, so there is little intrinsic conductivity. When an electron is removed (p-doping) from or added (n-doping) to a conducting polymer, polaron, and/or bipolron (dication) states are formed. When a great many bipolarons are formed, their energy states overlap at the edges, which creates narrow bipolaron bands within the band gap [14]. Both polarons and bipolarons can move along the polymer chain in an electric field and thus conduct electrical current.

1.2 Synthesis Methods

Polythiophene and its derivatives can be prepared by several methods which include electropolymerization, chemical polymerization (e.g., metal-catalyzed cross-coupling [15,16], metal halide methods [17]), and regioregular controlled polymerization (e.g., the McCullough [18] and the Rieke methods [19].

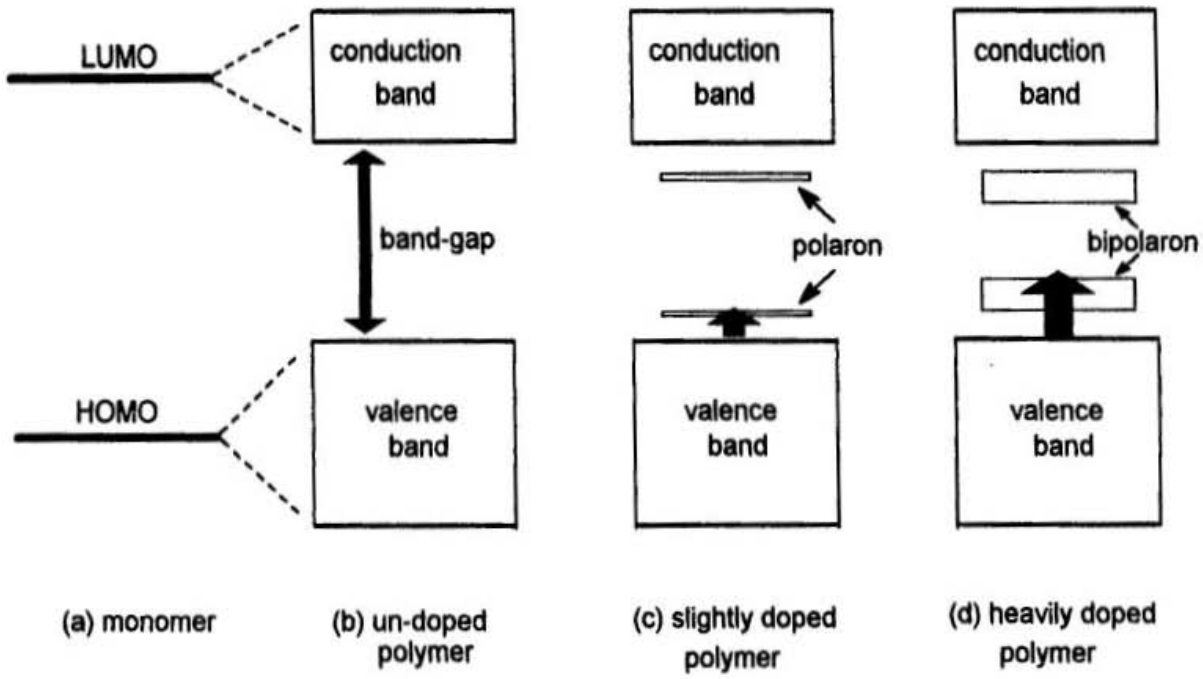


Figure 1.2 Schematic diagram of the evolution of the band structure of a conjugated polymer

1.2.1 Electrochemical Polymerization

Electrochemical polymerization of thiophenes are generally carried out in a nonaqueous solvent containing the monomer and an electrolyte salt under an inert atmosphere. Electropolymerization to produce poly(thiophene)s, PTs, involves many experimental variables such as the choice of solvent, concentration of reagents, temperature, nature of electrodes, and applied electrical conditions (e.g. potentiostatic, galvanostatic, recurrent potential sweeps and current pulses). Effects of these variables are summarized by Roncali [12]. Under optimum synthetic conditions, PT films can be prepared with enhanced effective conjugation and with conductivities reaching 2000 $S.cm^{-1}$ [12].

During electropolymerization, a monomer is first oxidized to its radical cation, then coupling of two radicals produces a dihydro dimer dication which leads to a dimer after loss of two protons and re-aromatization. Due to the applied potential, the dimer, which is more easily oxidized than the monomer, occurs in its radical form and undergoes a further coupling with another monomeric radical. Electropolymerization proceeds then though successive electrochemical and chemical steps until the oligomer becomes insoluble in the electrolytic medium and precipitates onto the electrode surface.

Besides the radical cation coupling mechanism mentioned above, an alternate

polymerization mechanism, coupling of radical cations with unoxidized molecules, has been suggested by a number of authors [20].

1.2.2 $FeCl_3$ Method

The $FeCl_3$ method is one of the most common chemical methods applied to the synthesis of poly(3-substituted thiophenes). The polymerization is proposed to proceed through a radical mechanism [21]. Firstly, 3-substituted thiophene is oxidized by $FeCl_3$ to form a monomer radical cation. The radical undergoes a coupling reaction with a monomer radical and yields a dimer radical which can be further oxidized by $FeCl_3$ to a neutral dimer. The dimer reacts with another monomer or another dimer, generating an oligomer and eventually a polymer chain. The byproduct HCl is evolved.

Although the $FeCl_3$ method decreases the occurrence of α-β' coupling in polyalkylthiophenes, the method gives variable results [22]. For example, molecular weights range from 54 K to 122 K for poly(3-octylthiophene)s even when formed under identical reaction conditions [23].

1.2.3 The McCullough Method

In 1992, McCullough and Lowe first reported the synthesis of regioregular head

(H)-to-tail (T) coupled poly(3-alkylthiophenes) (PAT) [18].This synthetic method regiospecifically generates 2-bromo-5-(bromomanesio)-3-alkylthiophene, which is then polymerized with catalytic amounts of Ni(dppp)Cl_2 using cross-couplings to give PATs with 98-100% HT-HT couplings. The PAT polymers can be prepared in yields of 44-69%.

1.3. Some Important Polythiophenes

1.3.1 Polythiophene (PT), Poly(2,2'-bithiophene) (PBT) and Poly(2,2':5',2''-terthiophene) (PTT)

Studies of polythiophenes as a new generation of conducting polymers started in the early 1980s. Before 1990, the emphasis on this polymer was to achieve high electrical conductivity by extending the effective conjugation length, minimizing defects caused by overoxidation and improving polymer morphology.

One strategy was the use of thiophene oligomers (e.g. 2,2'-bithiophene (BT) and 2,2':5',2"-terthiophene (TT)) in place of thiophene monomer for electropolymerization [24, 25]. Owing to their lower oxidation potentials [26], electropolymerization can be performed under milder condition [27]. Furthermore, since the thiophene rings are exclusively α-α' linked in the starting molecule, one could expect the resulting polymer to contain less α-β' defects than that prepared from thiophene [28].

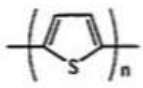
However, results from several groups [12, 24] have shown that the resulting polymers differ markedly from those prepared from the monomer. PBT and PTT (Figure 1.3) are usually obtained as powdery deposits with conductivities inferior by several orders of magnitude to PT (Figure 1.3). The best conductivity of PBT only reached at a few S cm^{-1}, while for PTT, it was in the range of 10^{-2} S cm^{-1}.

Electrochemical and spectroscopic properties of PT, PBT and PTT show that the lower conductivities of PBT and PTT are correlated to a decrease of the average length in the conjugated π system in the polymer. This limited conjugation can be explained by the decreased reactivity of the substrate (during polymerization), in other words, the stability of the corresponding radical cation of BT and TT increases, which causes a decrease or even in some cases a complete loss of polymerizability. This explanation is consistent with the limited electropolymerization of TT as shown by the fact that PTT contains large amounts of unreacted TT and hexathiophene oligomers [24]. In addition, the reactivities of the α and β positions becomes progressively closer with increasing chain length, thus increasing the number of α-β' couplings. This leads to a lower degree of conjugation in the polymer.

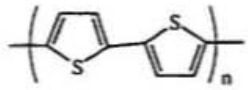
1.3.2 Polyalkylthiophenes

The poly(3-alkylthiophene)s (i.e., poly(3-methylthiophene) (PMT), poly(3-

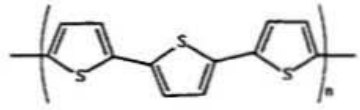
Unsubstituted Polythiophenes



Polythiophene [PT]

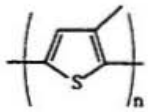


Poly(2,2'-bithiophene) [PBT]

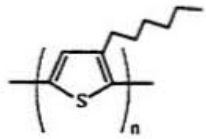


Poly(2,2':5',2"-terthiophene) [PTT]

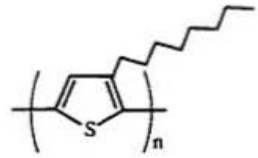
Polyalkylthiophenes



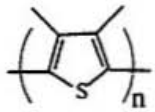
Poly(3-metylthiophene) [PMT]



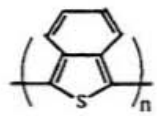
Poly(3-hexylthiophene) [PHT]



Poly(3-octylthiophene) [POT]

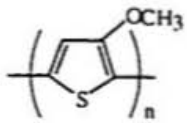


poly(3,4-dimethylthiophene)

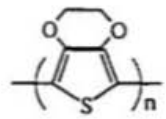


Polyisothianaphthene

Polyalkoxythiophenes



poly(3-methoxythiophene) [PMOT]



Poly(3,4-ethyldioxythiophene) [PEDOT]

Figure 1.3 Structures of thiophene-based conducting polymers.

hexylthiophene) (PHT) and poly(3-octylthiophene) (POT), etc.) (Figure 1.4) have attracted increasing interest since their synthesis in 1986. Owing to the presence of flexible hydrocarbon chains on the conjugated PT backbone, they display properties superior to unsubstituted polythiophenes, such as higher conductivities, better solubility in organic solvents and fusibility [15, 29].

Introducing an alkyl group at the β -position also reduces the probability of α-β coupling between thiophene units and leads to more stereoregular polymers [22]. No α-β′ coupling was observed for poly(3-butylthiophene) synthesized by metal-catalyzed cross-coupling polymerizations, nor for the PAT synthesized by the $FeCl_3$ method [22]. However, the PAT synthesized by these methods lack regioregularity. There are three relative orientations available when two thiophene rings are coupled between the 2 (α) and 5 (α′)-position. Namely, head-tail (HT), head-head (HH), and tail-tail (TT). This leads to a mixture of four chemically distinct triad regioisomers (trimers) when 3-substituted (asymmetric) thiophene monomers are employed. Irregularly substituted polythiophenes have structures where unfavorable HH couplings cause a sterically driven twist of the thiophene rings resulting in a loss of conjugation. On the other hand, regioregular, HT poly(3-substituted) thiophenes can easily access a low energy planar conformation, leading to highly conjugated polymers. In 1992, The first synthesis of regioregular HT coupled PAT was reported by McCullough and his coworkers [18]. The PAT synthesized by their method contained ~100% HT-HT couplings.

Disubstitution at the 3- and 4- positions of thiophene has appeared as an interesting method to synthesize perfectly stereoregular polymers by eliminating the possibility of α-β′ linkage. However, poly (3,4-dialky-thiophenes) (e.g., poly (3,4 dimethylthiophene, Figure 1.3) normally have higher oxidation potentials, high optical band gaps and lower electrical conductivities than mono-substituted polymers [30]. This can be explained by the higher steric hindrance between disubstituents grafted on consecutive structural units which distorts the conjugated π system, providing a considerable loss of effective conjugation. It was found however that the steric hindrance between neighboring cycloalkyl-substituted monomer units in the polymer chain (e.g., polyisothianaphthene, Figure 1.3), is not as severe as in the case of 3,4-alkyl-substituted compounds [22].

1.3.3 Polyalkoxythiophenes

Polyalkoxythiophenes (e.g., poly(3-methoxylthiophene) (PMOT), (Figure 1.3) have better solubility and fusibility properties than unsubstituent polythiophenes. Introducing an alkoxy group with oxygen directly attached to the thiophene ring results in a reduced bandgap of the polymer and/or increase in stability. In addition, these side chains can be used as molecular recognition units for chemical sensing or as arms for directed self-assembly of the polymer. However, short alkoxy chains on PT that had been synthesized chemically or electrochemically generally led to low molecular weight polymers and insoluble materials. To improve solubility, long chain alkoxy substituents and 3,4-

dialkoxyl substituents on the polythiophene backbone were introduced [24].

In 1991, poly(3,4-ethylenedioxythiophene) (PEDOT, Figure 1.3) was successfully produced. It shows not only high conductivity and a much lower bandgap, but also better environmental stability and a higher doping level than PT [31].

1.4 Traditional Analytical Techniques

Structure plays a dominant role in determining the physical properties of conducting polymers. Various analytical techniques have been used for polymer characterization. The traditional characterization techniques include electrochemical methods, chromatographic techniques, and spectroscopy.

1.4.1 Cyclic Voltammetry

Among the various electrochemical methods, cyclic voltammetry (CV) is a popular technique where the potential is linearly scanned up to a switching potential and then reversed to its initial value. It is often the first experiment performed for electrochemical study of a compound and its redox reaction. Its biggest advantage is rapid detection and characterization of the redox couples and it can yield important kinetic and mechanistic information about electrode reactions. It is also a popular technique for the

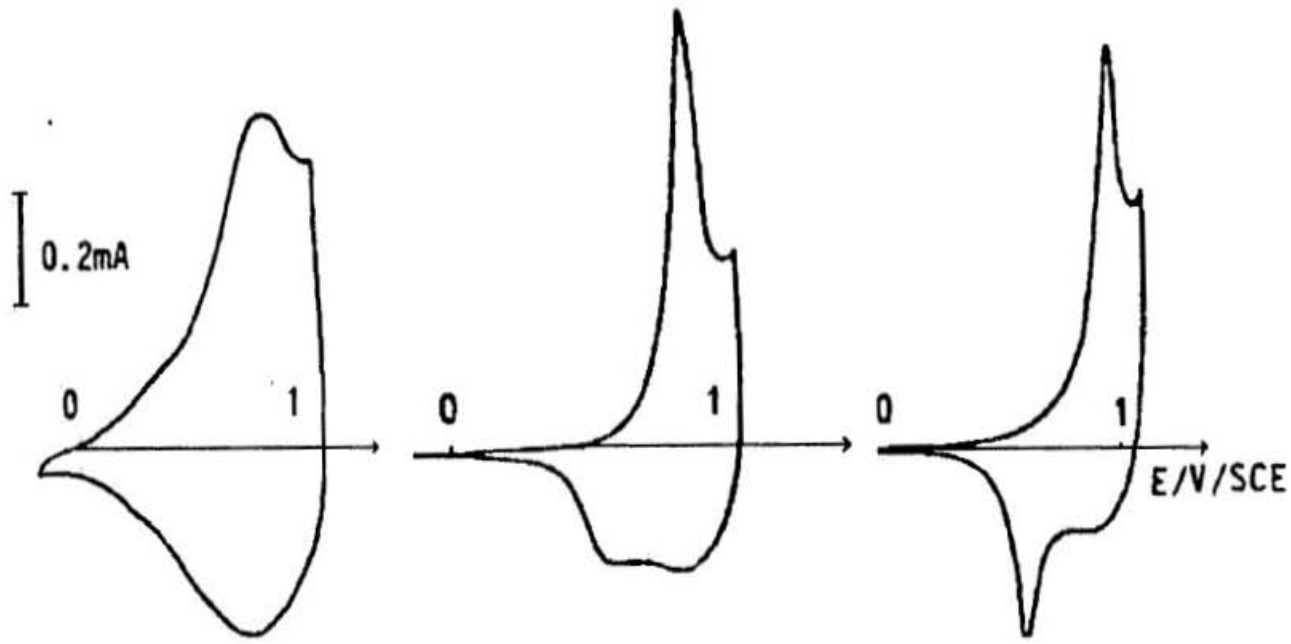
electropolymerization of conducting polymers. It can provide "in-situ" information about the oxidation behavior of the monomer and the progressive growth of the polymer observed from gradually increasing doping and de-doping currents when the potential is scanned repetitively over a suitable range.

In principle, the quality (i.e., conductivity, stability, charging capacity) of conducting polymers and the factors (i.e., the electrolytes, solvent, temperature, electrode material, nature of the monomer and its concentration), which affect the quality of conducting polymer polymerization as well as polymerization mechanisms can be investigated by CV. From the cyclic voltammogram, the cathodic charges indicate the amount of polymer deposited [32]. Peak width at half height of the oxidation wave (PWHH) reflect the distribution of conjugation chain length. For example, comparing cyclic voltammograms of PT, PBT and PTT, deposited on Pt electrodes under the identical conditions show that oxidation potentials of the substrates decreased when the chain length is increased (Figure 1.4). PWHH of the oxidation wave for PBT and PTT are about half that for PT, reflecting a narrower distribution of the chain lengths in PBT and PTT [33].

1.4.2 Spectroscopy

1.4.2.1 Ultraviolet-Visible (UV-Vis) Absorption Spectroscopy

The method of UV-Vis spectroscopy is perhaps the most widely used of all



(A) **PT** (B) **PBT** (C) **PTT**

Figure 1.4 Cyclic voltammograms of PT, PBT and PTT.

quantitative and qualitative analysis techniques for organic polymers. The absorption of ultraviolet or visible radiation generally results from excitation of bonding electrons. As a consequence the wavelengths of absorption peaks can be correlated with the types of bonds in the species under study. In conjugation systems, π electrons are delocalized by conjugation thus lowering the energy level of the π^* orbital and giving it less antibonding character. This results in absorption maxima shifts to longer wavelengths [34]. This characteristic "bathochromic shift" (red shift) with longer conjugation makes UV/Vis spectroscopy a useful method for conducting polymers since their quality is determined by their mean conjugation length.

In UV-Vis studies, absorption spectra are measured in solution or with polymers deposited on a transparent iridium tin oxide electrode. Roncali compared the UV-Vis absorption spectra of unsubstituted polythiophenes which were electropolymerized under the same conditions and found their maximum absorption to be 485nm, 475nm and 400nm for PT, PBT and PTT respectively [33]. This hypsochromic shift revealed a decrease of the mean conjugation length from PT to PTT, in agreement with electrochemical data.

In addition, a linear relationship between the anodic peak potential (E_{pa}) for the oxidation reaction values and λ_{max} values for the series pyrrole , bipyrrole, terpyrrole and polyprrrole were observed [35]. A similar linear relationship is also obtained for the α-α' coupled thiophene series. Using this method, the mean conjugation length can be

calculated. Conjugation lengths for electrochemically polymerized PT ranging from 15 to 20 thiophene rings were reported [36]. However, the relationship between the positions of λ_{max} and E_{pa} is not clear with methyl-substituted thiophene oligomers due to the steric hindrance imposed on the molecules by the methyl groups.

The steric interactions between substituents and the thiophene rings were investigated using UV-Vis absorption. Poly(3,4-dialkylthiophene)s (e.g., poly (3,4-dihexylthiophene) and poly(3-methyl-4-octylthiophene)) showed a blue shift in the UV-Vis absorption in comparison with mono-alkyl substituted PT. This is due to the fact that disubstituted polymers have non-planar conformations of the monomeric unit backbone resulting from steric interactions between the substitutents and the adjacent thiophene rings [37].

1.4.2.2 Vibrational Spectroscopy

Infrared (IR) and Raman spectroscopy are the two most common techniques used to study vibrational transitions. The IR spectrum arises from the absorption of radiation, the frequency of which is resonant with a vibrational transition, while the Raman effect results from inelastic scattering of photons leaving a molecule or crystal in a vibrationally excited state. The combination of IR and Raman spectroscopy extracts much of the useful information, due to their complementary nature. Although they can provide quantitative

information, qualitative analysis by comparison of spectral "fingerprints" (i.e., below 1400 cm^{-1}) with reference spectra libraries to identify unknown materials is used widely for conducting polymers. Appearance of new absorption frequencies and shifts in absorption frequencies and band broadening, have allowed overoxidation, stereoregularity, and conducting polymer modification to be studied [38, 39]. Conjugation length can also be calculated by selectively deuterium labeling at the α and β positions. Akimoto *et al* reported that the intensity ratio of the infrared C-H out-of-plane bending mode at 681-688 cm^{-1} for (2-substituted thiophenes) units to C-H out-of-plane bending mode at 784-792 cm^{-1} for (2,5-substituted thiophene) units is a clue to the degree of polymerization [40].

The vibrational spectra of conjugated materials have been the subject of many experimental and theoretical studies aimed at establishing structure-property correlations. Materials studied include pristine in the undoped, doped, and photo excited states. The spectroscopic manifestations observed in these three states are dramatically different and have required the development of new theoretical models for their interpretation. A excellent review in this topic has been published [41].

1.4.2.3 Nuclear Magnetic Resonance Spectroscopy (NMR)

With its rapid advances in instrumentation and experimentation, NMR has become an important method for material characterization and for the study of polymer structure-

property relationships. Solution NMR (^{1}H, ^{13}C) signals are obtained by measuring the magnetic moments of their hydrogen or carbon-13 atoms. Usually, ^{13}C NMR is complementary to ^{1}H NMR and is used mostly in characterization of the carbon skeleton of the polymers..

The usefulness of ^{1}H and ^{13}C-NMR techniques arises in part because the signals can be assigned to specific atoms along the polymer backbone and side chains and they are sensitive to small changes in the chemical structure of polymers, such as those that arise from polymer stereochemistry. These include defects such as branch crosslinks, and head-head (HH) and tail-tail (TT) regioisomers and other types of microstructure. For example, using proton NMR data, the content of HT-HT in PBuT, PHT and POT synthesized by the McCullough method are reported to be 93%, 98% and 97% respectively [42], while the content of HT-HT in polymers synthesized using $FeCl_3$ oxidant ranging from 70 to 80% was reported [43]. NMR thus confirms that conducting polymers of structurally high homogenity can be produced by the McCullough method.

Besides solution NMR techniques, solid-state NMR has been applied to conducting polymer characterization for those polymers which have poor solubility. Solid-state NMR can be acquired in the high-resolution or wide-line mode, yielding different but complementary information. Chemical structures of PT and PMT in their solid state have been established using high resolution solid-state ^{13}C-NMR [44].

1.4.3. Gel permeation Chromatography (GPC)

Among chromatographic techniques, GPC is most widely used in solvent-soluble polymer analysis. It is capable of characterizing very high molecular weight film and fibre polymers up to 10^6 daltons [45]. The smaller molecules which are able to pass into most of the pores have a relatively long flow path through the column. The larger polymer molecules which are excluded from all but the largest of pores have a shorter flow path, and elute first. Using this method, molecular weight distributions can be determined. For example, the molecular weight distribution of PAT determined by GPC using different detectors ranging from 68-175K (RI), 77-146K (UV-Vis), and 204-398K (light scattering) were reported [22]. However, molecular weights estimated by GPC are significantly higher than the true values due to the use of unsuitable polystyrene calibration procedures. Using proper constants (e.g., Mark-Houwink) for calibrating the GPC column leads to more accurate determination of molecular weight of PHT [46]. However, this correction technique is limited to information related to stereoregularity and cross linking.

Gas chromatography (GC), which is usually used in volatile and thermally stable small organic compound analysis, is not suitable as a chromatographic technique for polymer studies. However, when it is coupled with pyrolysis, it becomes a very elegant technique for structural identification and quantification of polymer composition as described below.

1.5 Analytical Pyrolysis

Pyrolysis is a high temperature process which involves the thermal degradation of materials in an inert atmosphere. Pyrolysis can be used either for the disposal of waste materials and / or in the production of energy or commercially useful chemicals (applied pyrolysis) or used for the chemical characterization of materials by qualitative and quantitative analysis of the pyrolysis products (analytical pyrolysis). As well, analytical pyrolysis is well suited for mechanistic and kinetic studies in thermal degradations (fires) and in the production of fire-resistant materials.

Analytical pyrolysis (Py) is defined as the characterization of a sample by a chemical degradation reaction in an inert atmosphere induced by thermal energy. When the pyrolysis unit is coupled to sophisticated analytical instruments (i.e., GC, GC/MS) for the separation and/or identification of the pyrolysis products, the application of this technique for chemical characterization increases significantly. Two types of pyrolysers (i.e., resistively heated pyrolyser and Curie-point pyrolyser) have been commercially developed providing highly reproducible thermal treatment of the sample, making the application available to quantitative analysis [47]. In quantitative analysis, controlling parameters which effect the reproducibility are sample size, pyrolysis temperature (T_{py}) and carrier gas velocity. Good heat transfer and rapid heating of the pyrolysis element are essential in achieving reproducibility. With sample size increase, the probability of secondary reactions

increases due to slow heat transfer within the sample. Small sample sizes, less than 500µg was recommended [48]. Optimization of the pyrolysis temperature is a very important step as well. In Py-GC, a high carrier gas velocity is required to quickly remove the pyrolysates from the heated zone and prevent high boiling products from condensing. But the carrier gas should also be controlled as to not affect the temperature profile [49].

1.6 Analytical Pyrolysis In Polymer Characterization

Modern analytical pyrolysis is now extensively practiced using Py-MS and Py-GC (or Py-GC/MS), where the characterization of the original sample is carried out through on-line analysis of the resulting complex pyrolysates. These techniques have found wide application in polymer characterization.

1.6.1 Py-MS

Py-MS is a rapid and simple method and is often used to obtain a "fingerprint" for identification of a given material. It has two modes, namely direct Py-MS and indirect Py-MS. In direct Py-MS, pyrolysis is under the vacuum conditions of the MS source. Pyrolysis and ionization are simultaneous [50]. This minimizes secondary reactions and offers high mass molecular fragment analysis. In indirect Py-MS, only volatile and stable decomposition products isolated off-line can be identified by MS. Extensive fragmentation

occurs in the ion source (EI) of the quadrupole and is a serious drawback to high mass fragment analysis. Two approaches, reducing ionization energy and employing a soft ionization method (CI, FI, FAB), have been applied to minimize low mass electron-impact-induced fragments [51].

High cost, difficult identification of isobaric compounds and isomeric products and the difficulties in relating the mass peak distribution of the pyrolysis products to the structure of the polymer limits the PY-MS applications. In these cases, Py-GC-MS can show major advantages.

1.6.2 Py-GC and Py-GC-MS

The Py-GC and Py-GC-MS techniques allow for the rapid volatilization, separation and identification of pyrolysis products [49]. Detailed information about individual pyrolysates can be obtained. In Py-GC and Py-GC-MS, high resolution gas chromatographic separation is carried out in a capillary column, while, improved mass spectrometric identification can be achieved either by soft ionization methods or by tandem MS (MS/MS). Compared with Py-MS, Py-GC-MS has the ability to separate isomers and produce excellent quantitative analysis of mixtures. With a highly specific detector, quantitation can be reach at very low levels [48]. These strengths make it a powerful technique for polymer characterization. Specifically, it can provide stereochemical and

quantitative information about polymers: However, Py-GC and Py-GC-MS have difficulty detecting very high molecular weight fragments, very polar fragments and unstable pyrolysates [49].

1.6.3 Polymer Characterization

Overall, Py-MS and PY-GC/ Py-GC-MS have their own advantages and disadvantages. The choice of a technique clearly depends upon the facilities available and the nature of polymers to be analyzed. They are complementary to each other. The following summarize the major applications by these two techniques for characterization of polymers.

(1) Qualitative analysis involving fingerprint identification by comparison of a pyrogram from an unknown sample with those from standard materials and component identification by a comparison of the retention times of standard compounds or correct interpretation of mass spectra of characteristic pyrolysis fragments [49].

(2) determination of copolymer compositions by identification of hybrid dimers and trimers which are observed in the pyrogram of a copolymer [52, 53].

(3) assessments of polymer taciticity by determination of isomers which are resolved by capillary column chromatography. Such products depend upon the stereochemistry of the polymer [54,55].

(4) estimation of the degree of polymerization by analysis of the relative intensities of the

end groups [56, 57].

(5) deduction of polymer thermal decomposition mechanisms by relating the polymer units to the compounds evolved by pyrolysis [58, 59].

For conducting polymers, however, few analysis have been done by pyrolysis techniques. Vatansever studied the thermal behavior using Py-MS of composites of polythiophene and polyamide prepared by mechanical blending and electrochemical synthesis of polythiophene onto an electrode coated with polyamide [60]. In addition, Xie and Liu investigated the thermal decomposition processes of poly(thio-1, 4-pheneylene), polythiophene (PT) and polyaniline (Pan) by using direct pyrolysis EI or CIMS and direct Py-MS/MS. They concluded that all three conducting polymers undergo free radical decomposition during pyrolysis whereas only PT and Pan pyrolyze into linear oligomers [50]. Another group investigated the thermal degradation products of four polythiophene models, (i.e., poly(3-octylthiophene), poly(3-octyl)-2,2′-bithiophene, poly(3-(4-octylphenyl)thiophene, poly(3-4-octylphenyl-2,2′-bithiophene), and conclude that the rate of formation of H_2S was influenced by the chemical environment of the thiophene ring [61]. For conducting polymers, the use of analytical pyrolysis has been very limited. No stereochemistry studies of conducting polymers using analytical pyrolysis was found.

1.7 Objectives

Although analytical pyrolysis is a powerful technique for polymer characterization, very little work in this area has been done on conducting polymers. Our work has focused on the application of analytical pyrolysis to the characterization of thiophene-based polymers and to improve understanding of their thermal behavior. Conducting polymer samples used in our studies include unsubstituted poly(thiophene)s (i.e., PT, PBT, and PTT), poly(3-alkylthiophene)s (i.e., PMT, PHT, POT) and poly(alkyloxythiophene)s (i.e., PMOT and PEDOT).

The specific objectives are:

(1) to optimize the PY-GC-MS method and its experimental conditions (e.g., choice of column, pyrolysis temperature, separation conditions, interference reduction, etc.) for analysis of conducting polymers;

(2) to better understand the relationship between thermal behaviors of unsubstituted polythiophenes and their conducting properties;

(3) to study the microstructures of unsubstituted poly(thiophene)s, poly(3-alkylthiophene)s and poly(alkyloxylthiophene)s;

(4) to determine the thermal degradation pathway of poly(3-alkylthiophene)s using fractionated pyrolysis.

Chapter 2

Experimental Section

2.1 Chemicals and Reagents

Various thiophene precursors were used to synthesize conducting polymer samples analyzed in this study. Thiophene (Th), (99%), 2-2'-bithiophene (BT), (97%), 2,2':5',2"-terthiophene (TT), (99%), 2,2':5',2":5",2"'-quaterthiophene (TETT), (obtained from University of Waterloo), 3-methoxythiophene (MOT), (98%), and 3-hexylthiophene (99%) were purchased from Aldrich and used as received. The monomer of PEDOT, a sample of 3,4-ethylenedioxythiophene (EDOT) was donated by the Bayer Corp. (Pittsburgh).

Three diads (i.e., structural dimers) and four triads (i.e., structural trimers) of 3-hexylthiophene, namely 3,3'-dihexyl-2,2'-bithiophene, 4,4'-dihexyl-2,2'-bithiophene, 3,4'-hexyl-2,2'-bithiophene, 3,4',3"-trihexyl-2,2':5',2"-terthiophene, 4,4',3"-trihexyl-2,2':5'2"-terthiophene,3,4',4"-trihexyl-2,2':5',2"-terthiophene,4,4',4"-trihexyl-2,2':5',2"-terthiophene, were kindly provided by Dr.G.Barbarella and coworkers (University of Bologna, Italy) as reference standards to identify the pyrolytic oligomers produced from poly(3-hexylthiophene).

In electropolymerization experiments, the electrolyte, tetraethylammonium tetrafluoroborate (Et_4NBF_4) was used as purchased from Caledon laboratories. Anhydrous ferric choride ($FeCl_3$, Fluka, 98⁺%) was employed as the oxidant in chemical synthesis of poly(3-methoxythiophene) and poly(3-hexylthiophene).

Acetonitrile (LiChrosolv, LC grade, 99.75%) was purified first by running through an alumina column and then distilled under argon over calcium hydride powder (CaH_2, ~ 40 mesh, 90-95%) as desicant before use. Acetonitrile was used as the solvent for all electropolymerization experiments.

Solvents including acetone (spectrograde, Caledon, 99.5%), methanol (HPLC grade, Sigma-Aldrich, 99.9⁺%), and acetonitrile (prepared above) were used as the washing solvents to clean samples and as extraction solvents to remove starting materials from produced polymers.

2.2 Conducting Polymer Samples

2.2.1 Purchased Samples

Poly(3-alkylthiophene)s including poly(3-octylthiophene) (Polysciences) and poly(3-methylthiophene) (Polysciences) were analyzed as purchased. Poly(3-hexylthiophene) (Aldrich) was analyzed after sample cleanup (Section 2.2.5).

2.2.2 Electrochemical Synthesis

A Pine Instrument RDE4 potentiostat, computer CC_1 program and a conventional three-electrode cell (50ml) were used for electropolymerization. The working electrode (Pt plate, 2 cm^2) was cleaned by heating to a red glow in the flame of a Bunsen burner. The counter electrode Pt wire was polished with slurries of alumina polishing powder followed by rinsing thoroughly with distilled water and acetonitrile. The reference electrode was a SCE. In all experiments, the concentration of electrolyte, Et_4NBF_4 was 0.1 M in 10ml acetonitrile. Before electropolymerization, the solution was purged with Ar for 5 min to remove oxygen. All electropolymerizations were performed under Ar.

Polythiophene (PT), polybithiophene (PBT) and polyterthiophene (PTT) were galvanostatically electropolymerized from solutions of thiophene (0.1 M), bithiophene (0.1 M) and terthiophene (0.03 M) with a current density of 0.5 mA/cm^2 for 2 hr, 1 hr and 40 min, respectively. The deposited polymers were then reduced by setting the potential at 0.0 V in potentiostatic mode. The resulting polythiophenes were washed three times each with acetone and acetronitrile.

The overoxidized PT was electropolymerized from a solution containing 0.1 M thiophene, 0.1 M Et_4NBF_4 and 15 µl H_2O per 10 mL of solution under constant current of 1 mA/cm^2 for 1 hr, then reduced and washed as described above.

The synthesis conditions for PEDOT was similar to that for PT, except that the reduction potential was set at -1.0 V.

2.2.3 Chemical Synthesis

Poly(3-methoxythiophene) was chemically synthesized from 0.15 M 3-methoxythiophene in 10 mL acetronitrile by mixing with ten times the molar amount of $FeCl_3$ (oxidant) in enough acetronitrile and magnetically stirred for 6 hr. After polymerization, the precipitated polymethoxythiophene was reduced using 0.1 M thiosulfate solution, then washed thoroughly with distilled water until all the inorganic salts were removed and finally washed with acetronitrile four times and dried in vacuum.

Poly(3-hexylthiophene) was prepared by mixing of 0.01 mol of 3-hexylthiophene in 40 mL chloroform with 0.04 mol $FeCl_3$ in 100 mL chloroform. The reaction mixture was stirred overnight at room temperature and then worked up with methanol. The impurities were extracted from the polymer by a Soxhelet apparatus using methanol then acetone till the extraction solvent became colorless. The remaining polymer was dried in vacuum.

2.2.4 Successive Electopolymerization of Unsubstituted Polythiophenes

Successive polymerization means that individual polymer samples were produced

repeatedly, from the same initial monomer solution under identical electropolymerization conditions (described in section 2.2.2). After the first electropolymerization, there are thiophene oligomers in solution formed from the previous experiment as well as thiophene monomers which subsequently are used as substrate for the next polymerization on a new Pt electrode. These resulting polymers of PT, PBT and PTT were examined to observe the effect of oligomer polymerization from solution on the structure of the polymers.

2.2.5 Polymer Sample Cleanup

All conducting polymer samples were washed three or four times each with acetone and acetonitrile, and then pretreated by 300°C thermal cleaning to remove monomers and oligomers remaining trapped in the polymer. (In initial experiments, at low pyrolysis temperatures it was found that some of the starting materials were still present with the polymer.) The pre-heated polymers remained unaffected. Therefore, the method of heat pretreatment at 300°C before pyrolysis at higher temperature was used to eliminate the presence of starting material in the resulting pyrograms.

The starting material, 2,5-dibromothiophene was observed in the pyrogram obtained from poly(3-hexylthiophene) purchased from Aldrich Chemicals. This polymer was successfully cleaned four times each with acetone, methanol, acetronitrile for half an hour using ultrasonic cleaning. Only a small amount of 2,5-dibromothiophene remained.

2.3. Analytical Pyrolysis

2.3.1 Pyrolysis Unit

As shown in Figure 2.1, the pyrolysis apparatus (model 120, Chemical Data System) consists of a pyroprobe, heated interface and a control box (not shown). The control box is used to adjust the pyrolysis temperature, the interface temperature and the rate of temperature rise. The heated interface was attached to the GC injector port using a 3 cm long stainless steel universal needle assembly (Chemical Data System). The pyroprobe is fitted with a Pt wire coil. About 200 μg of sample was placed in a quartz tube, (20mm×2mm i.d), the sample secured with plugs of quartz wool and inserted into the center of the Pt wire coil. The coil was heated rapidly to a predetermined T_{py}, and the pyrolysates swept by GC carrier gas (He, ultra pure) onto the GC column. The pyrolysis conditions are listed in Table 2.1.

Two-step pyrolysis experiments were conducted on unsubstituted polythiophenes and poly(3-alkylthiophene)s. Unsubstituted polythiophenes were first pyrolyzed at 300°C in order to remove starting materials which were trapped in the polymer matrix, and then pyrolyzed at 900°C for polymer analysis. The poly(3-alkylthiophene)s were first pyrolyzed at 600°C and then at 900°C in order to investigate their thermal degradation pathway.

2.3.2 Py-GC-MS

In chromatography, a DB-1 column (100% dimethyl polysiloxane, 23 m × 0.25mm id) and a DB-5 column (5% phenyl, 95% dimethyl polysiloxane, 23m × 0.25mm id) columns were examined in order to optimize the chromatographic resolution of the pyrolysates for the range of conducting polymers analyzed. Results revealed that the non-polar DB-1 column was insufficient to resolve the low molecular weight products such as H_2S and CS_2 and the peaks of the oligomeric pyrolysates were broad. In contrast, the slightly polar DB-5 column was able to separate pyrolysates from gaseous to higher oligomer products with good resolution and good peak symmetry. The Py-GC-MS conditions are given in Table 2.1.

Semi-quantitative analysis of selected pyrolysates was accomplished by GC-MS analysis in SIM (selected ion monitoring) mode where the mass spectrometer was set to scan for only selected oligomer parent ions. Using the SIM mode also provided good base line resolution and higher sensitivity[49]. The HP chemstation software was used to integrate the chromatographic peaks.

2.3.3 PY-GC-FID

Py-GC-FID analyses were performed on PT, PBT and PTT in order to accurately calculate the amount of monomers, thiophene, BT, and TT which were incorporated

(trapped) in the polymers after polymerization. Very little thiophene was found in PT. Standard calibration curves were prepared from solutions of BT and TT using chloroform as solvent.

Table 2.1 PY-GC-MS conditions

Apparatus	Model	Conditions
Pyrolyzer	CDS pyroprobe 120	Temp rise time: 8 ms Pyrolysis time: 10 s Interface temp: 250 °C
Gas Chromatography	Hewlett Parkard 5890 GC	Injector temp: 300°C Column: DB-5 (23m × 0.25 mm id) Column temp: 350 °C (3 min), 15 °C / min, 300°C (4 min) Detector temp: 300°C Split ratio: 25: 1 Column pressure: 20 psi (UHP He)
Mass Spectrometry	Hewlett Parkard 5971	Ionization energy: 70 eV Ion source temp: 190° C Scan range: 35-600 amu Scan rate: 1.5 scans / s

A pyroprobe 120 was mounted on a GC (Varian 3700) injection port. A flame ionization detector was employed. A Hewlett Packard HP 3395 integrator was used to plot the chromatogram and to integrate the chromatographic peaks. The GC conditions were

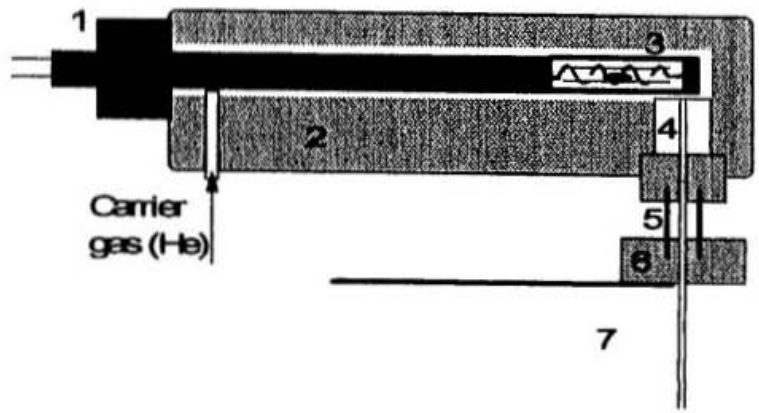
identical to that used in Py-GC-MS studies except the split ratio was changed to 10:1 and the DB-5 column length was 30 m.

2.3.4 FTIR

Infrared (IR) spectra were recorded as KBr pellets using a Mattson Polaris FTIR instrument. IR spectra were obtained from pressed discs of mixtures of small quantities of samples (PT, PBT , PTT and overoxidized PT) with about 10 mg of KBr. IR spectra were used to identify particular functional groups and to obtain information on the degree of polymerization.

2.3.5 NMR

Poly(3-hexythiophene)s solutions (~ 3 mg / mL $CDCl_3$) were examined using NMR. ^1H NMR spectra were obtained on a General Electric GE 300-NB (300MHz) instrument using TMS (δ = 0.0 pm) as the internal reference in $CDCl_3$. Number of acquisitions was 160. Solubility of PHT was very low.



1. Probe with platinum coil
2. Heated interface
3. Probe tip with conducting polymer samples inside in quartz tube
4. Capillary column threaded into interface
5. Steel connecting tube
6. Modified injector port
7. GC oven

Figure 2.1 Pyroprobe interface and probe attached to GC

Chapter 3

Py-GC-MS Analysis of Conducting Polymers

3.1 Optimization of Pyrolysis Temperature

During pyrolysis, chemical bonds are broken and molecules degrade into smaller fragments which are characteristic for the sample being pyrolyzed. However, besides primary reactions, secondary reactions may also take place. Usually at higher pyrolysis temperatures secondary reactions increase and smaller and less characteristic fragments are formed. Therefore, the first concern in analytical pyrolysis is to use a precisely controlled and optimum temperature for analysis.

In this study, pyrolysis temperatures (T_{py}) for conducting polymer analysis were optimized to obtain good yields of structurally-informative monomer, dimer and trimer products. Pyrolysis temperatures ranging from 300 to 1400°C were investigated for each type of polymer. Minimization of secondary reactions was also considered. As a way of observing trends, temperature profiles were constructed comparing yields of monomer, dimers or trimers with pyrolysis temperature.

Figure 3.1 shows the pyrolysis temperature/yield profile of poly(3-methoxythiophene). The yields of dimer and trimer are highest at T_{py} = 650°C, although the maximum yield of monomer occurred at T_{py} = 850°C. At this later temperature the yields of the other products are too low. Therefore, the optimum pyrolysis temperature for poly(3-methoxythiophene) was selected to be 650° C. Similar analyses were performed for the other 3-substituted polythiophenes. Poly(3-hexylthiophene) (Figure 3.2) and poly(3-octylthiophene) (Figure 3.3) gave optimum T_{py} values of 600 to 700°C.

In the case of unsubstituted polythiophenes, polyterthiophene (PTT) was selected to illustrate the temperature profile for this class of conducting polymer. Figure 3.4 shows that the highest yields of monomer, dimer, trimer and tetramer produced from PTT occurs at 1,150°C. However, when T_{py} is higher than 1,050°C, large quantities of elemental sulfur (S_8) appeared in the pyrolysates indicating that secondary reactions are very significant. From a mass spectrometer maintenance point-of-view introducing sulfur into the ion source damages the instrument source. Therefore, pyrolysis at 900°C, a temperature at which reasonable yields of oligomers still occur, was chosen as T_{py} for PTT. In order to compare the thermal behavior of unsubstituted polythiophenes. The same T_{py} = 900°C was chosen for PT and PBT as well.

Table 3.1 lists the selected T_{py} used for each conducting polymer analyzed in this study. Unless otherwise indicated, these T_{py} were used throughout the experimental work.

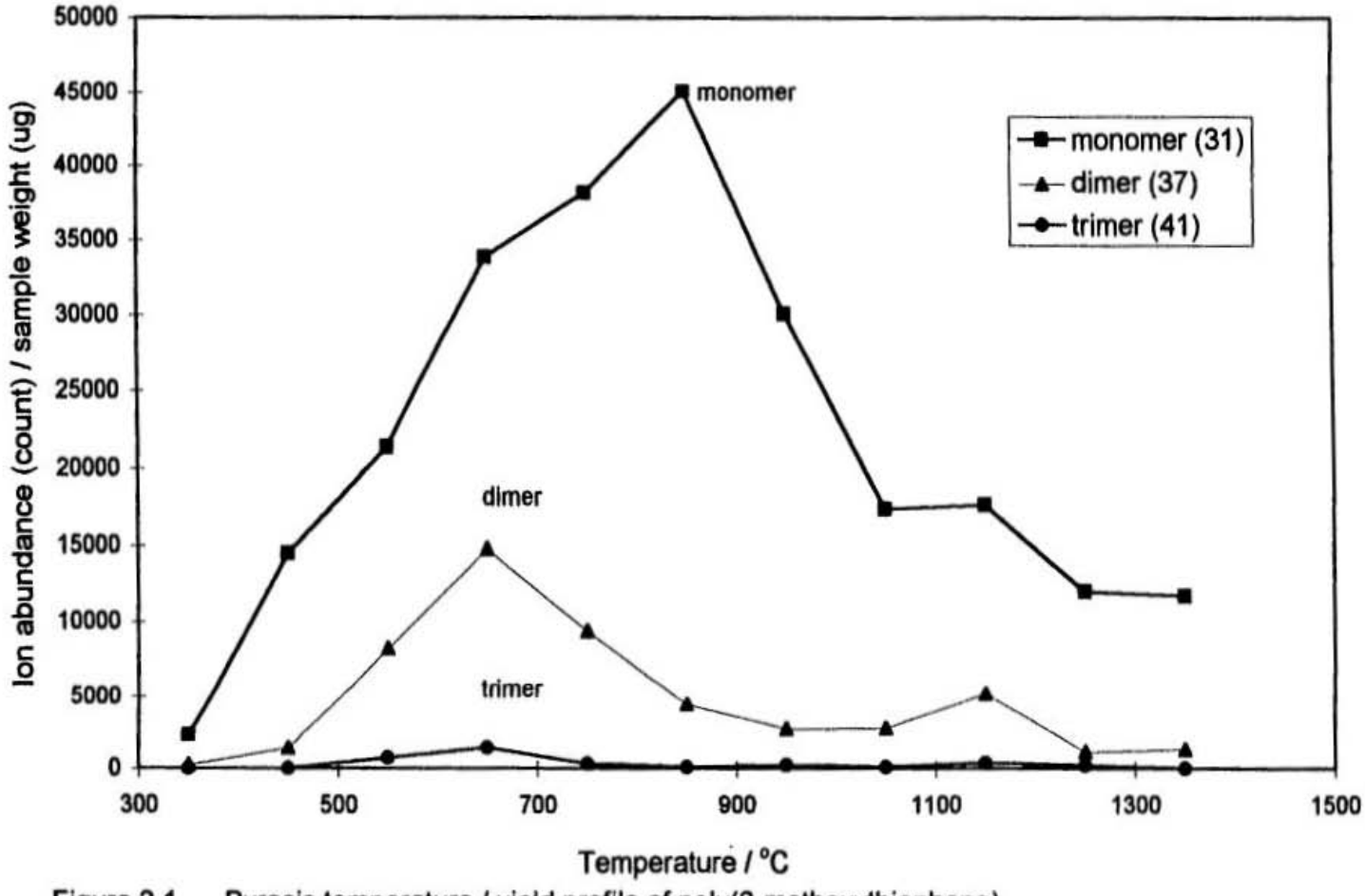


Figure 3.1 Pyrosis temperature / yield profile of poly(3-methoxythiophene).
The identities of the products are listed in Table 3.3. Ion abundances are measured in SIM mode

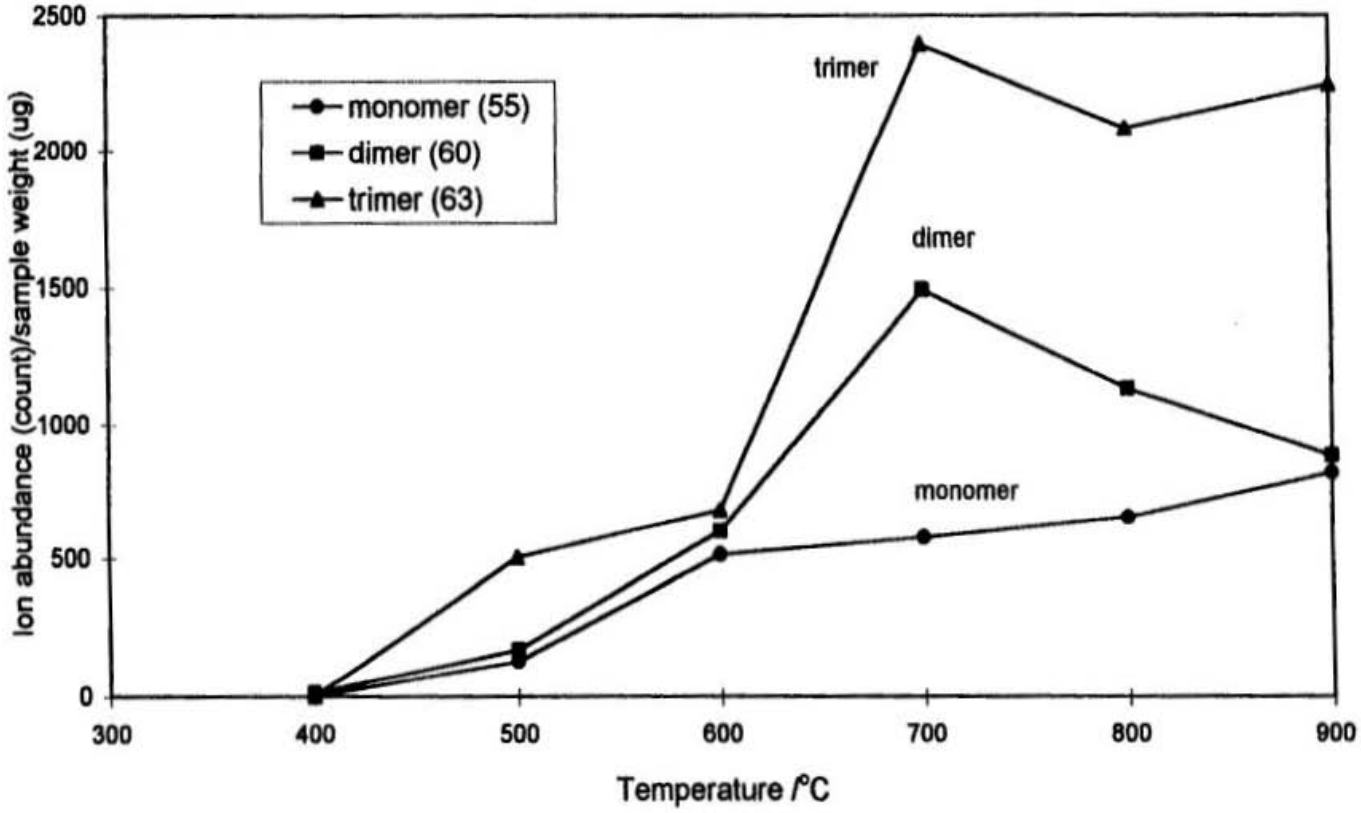


Figure 3.2 Pyrolysis temperature / yield profile of poly(3-hexylthiophene).
The identities of the products are listed in Table 3.5. Ion abundances are measured in SIM mode

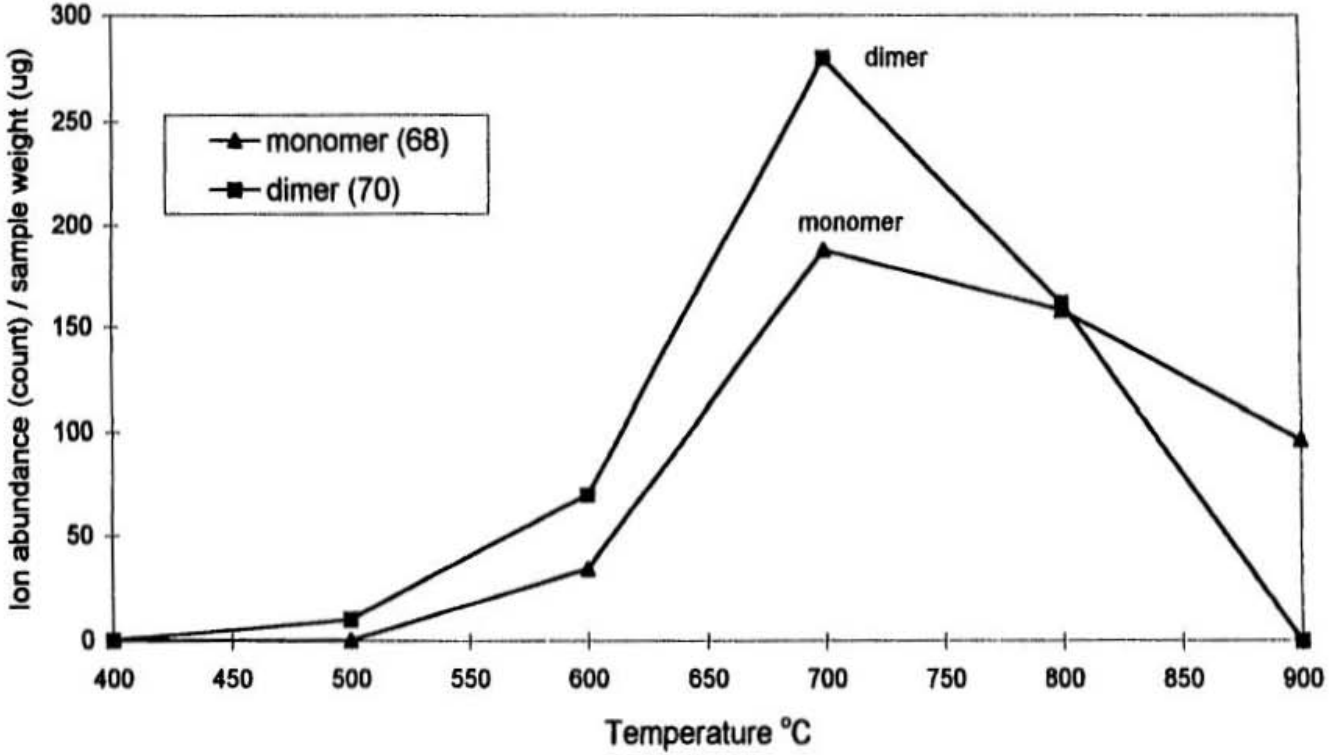


Figure 3.3 Pyrolysis temperature / yield profile of poly(3-octylthiophene).
The identities of the products are listed in Table 3.6. Ion abundances are measured in SIM mode.

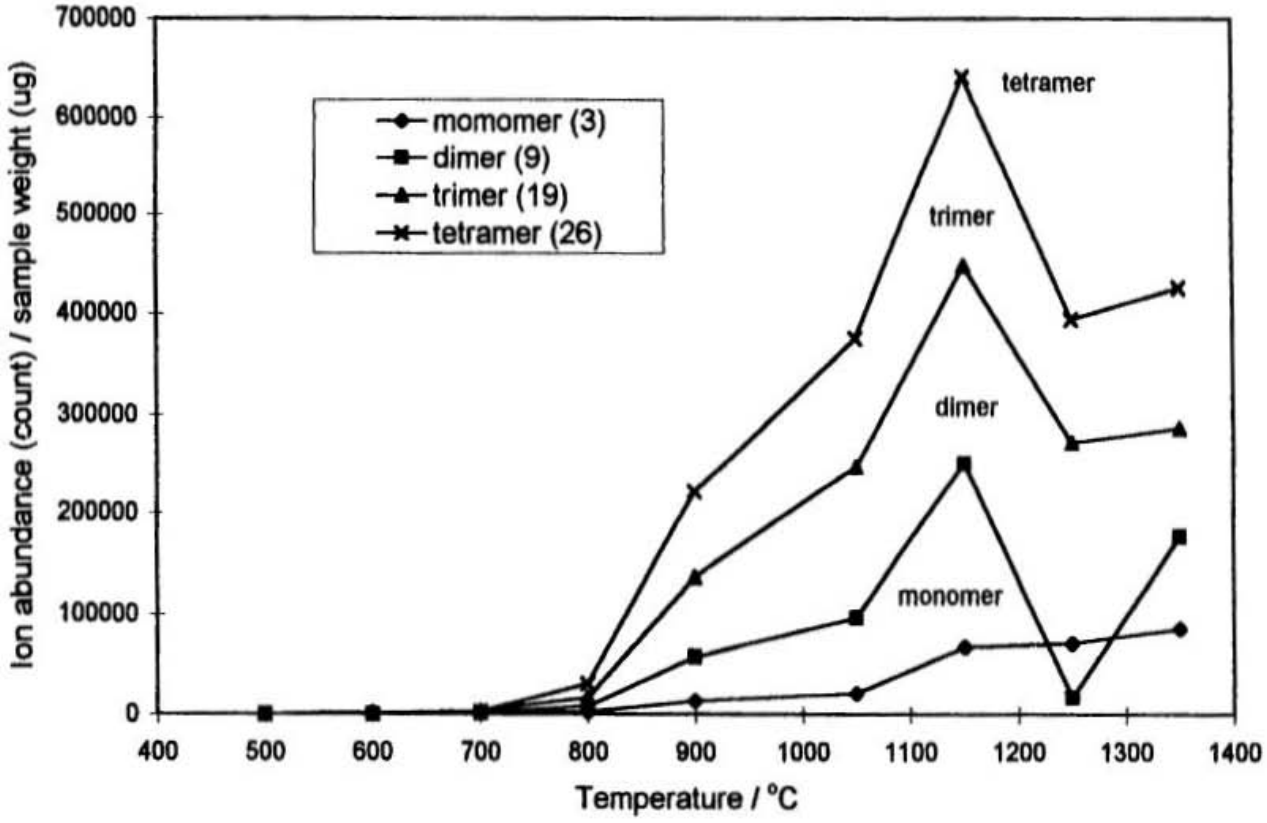


Figure 3.4 Pyrolysis temperature / yield profile of polyterthiophene.
The identities of the products are listed in Table 3.2. Ion abundances are measured in SIM mode.

The GC-MS conditions remained constant as described in the experimental section.

Table 3.1 Summary of the optimum pyrolysis temperatures for polythiophenes

Conducting polymer	T_{py}
polythiophene	900°C
polybithiophene	900°C
polyterthiophene	900°C
poly(3,4-ethylenedioxythiophene)	900°C
poly(3-methylthiophene)	900-1050°C
poly(3-methoxythiophene)	650°C
poly(3-hexylthiophene)	600-700°C
poly(3-octylthiophene)	600-700°C

3.2 Reproducibility

Reproducibility is important in both qualitative and quantitative analysis of polymers. In experiments, quantitative analysis was performed using Py-GC-FID to calculate the amount of bithiophene and terthiophene oligomer incorporated in electrochemically-deposited PBT and PTT, respectively. Semi-quantitative analysis was conducted using Py-GC-MS (SIM) in order to compare thermal behaviors of the unsubstituted polythiophenes, (i.e., PT, PBT and PTT), and to optimize T_{py} for the various

conducting polymer samples.

In Py-GC-FID studies, the precision of the analysis was examined by triplicate analysis of various concentrations of bithiophene (BT) and terthiophene (TT) solutions. The relative standard deviation (RSD) was found to be 7% for BT and 0.4% for TT. It is believed that the higher volatility of BT increased the RSD of the analysis. For triplicate analysis of polymeric samples the RSD ranged from 2-4 %.

In thermal behavior studies of PT, PBT, and PTT (Chapter 4), the reproducibility was examined by triplicate analysis of these polymers at their optimum pyrolysis temperatures. The RSD varied with different pyrolysates and with different conducting polymers. But the RSD of relative % yields for most pyrolytic products, (e,g., H_2S, thiophene, bithiophene, terthiophene, and tetrathiophene) was less than 10%. Products, such as CS_2, methylthiophene, methylbithiophene, and methylterthiophene had higher RSD values of approximately 15%. For the purpose of relative comparisons among polymeric samples these RSD values are satisfactory. It is likely that RSD in analysis of polymers arises from sample inhomogeneity.

In order to achieve good reproducibility, besides stringent control of all analytical parameters, the sample size is very important. A sample mass of 200 μg was chosen, large enough to represent the whole sample, but also not too large to affect heat transfer during

pyrolysis. Results which show trends of differences among samples are usually much more significant than the RSD in analysis. However, in the pyrolytic study of successive polymerization (Chapter 4), the RSD of relative intensities of some of the pyrolytic products is large due to the fact that it was difficult to reproduce the conditions of electrochemical polymerization, particularly the concentration and chemical nature of oligomers present in solution. Fortunately, the relationship between the pyrolytic yield and the quality of polymer could still be seen.

In the pyrolysis temperature optimization studies, only a single analysis for each temperature was needed to obtain a satisfactory trend. But in one case, poly(3-octylthiophene) was analyzed in triplicate to check reproducibility. The results showed that the RSD for oligomeric products, including dimer isomers ranged from 2-8 %, an acceptable value for semi-quantitative analysis. Also, it is well known that the reproducibility of electrodeposition of conducting polymer films is poor, even under strict control of all experiment parameters and conditions [14].

3.3 Pyrolysis Studies on Unsubstituted Polythiophenes

Pyrograms of polythiophene, polybithiophene and polyterthiophene are shown in Figure 3.5. Identified pyrolysis products are listed in Table 3.2 and selected structures are shown in Figure 3.6. Identification of most compounds was provided by comparing their

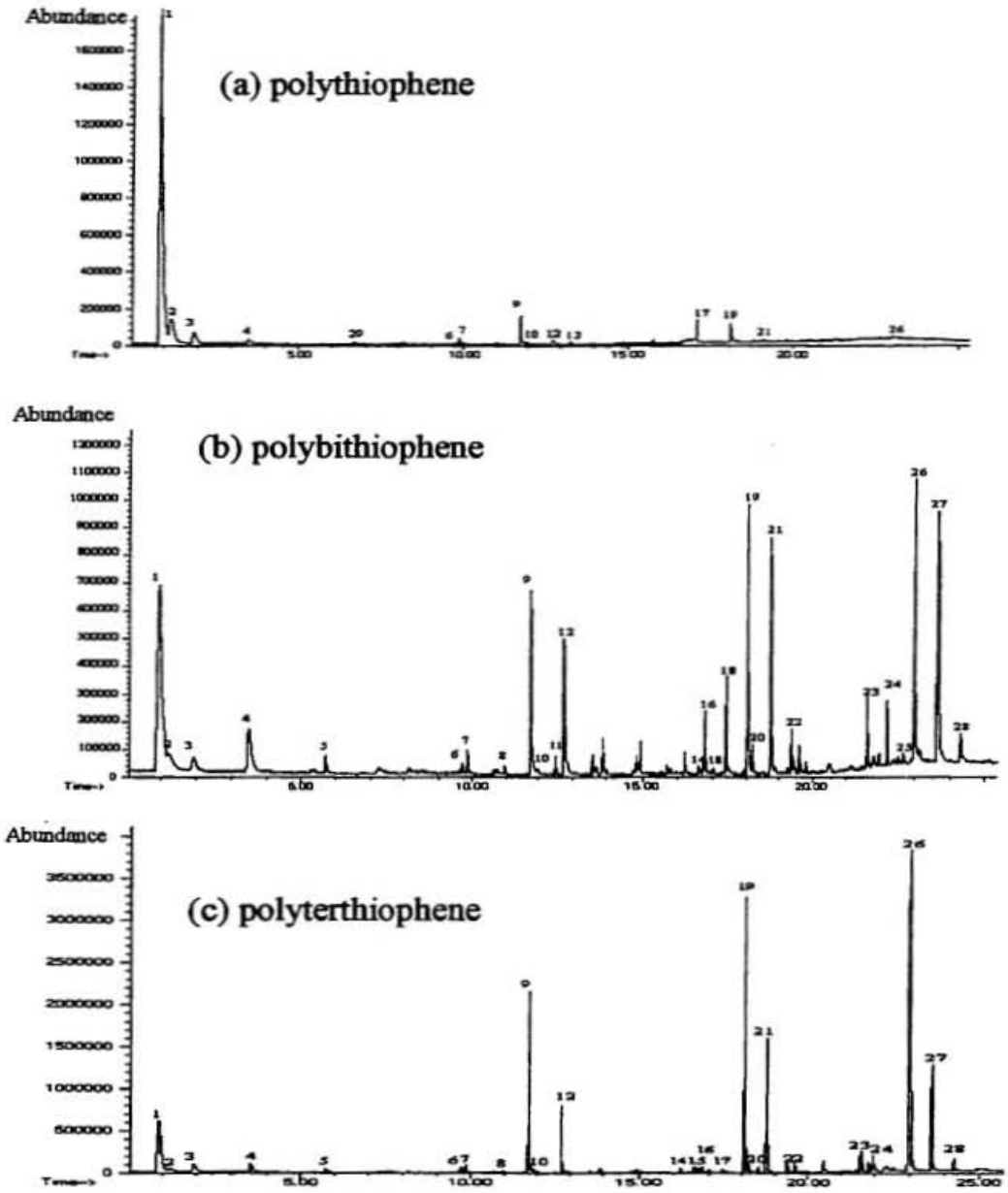


Figure 3.5 **Comparison of TIC pyrograms of (a) polythiophene, (b) polybithiophene and (c)polyterthiophene.**
The identities of the numbered peaks are listed in Table 3.2. Ion abundances are measured in Scan mode.

Table 3.2 Identification of products in the pyrogram of unsubstituted polythiophenes.

No.	RT.[r]	M.W.[m]	Structure[s]	No.	RT.[r]	M.W.[m]	Structure[s]
1[t]	0.93	34, 48, 64	H_2S, CO_2, SO_2	15[t]	16.72	222	*see Figure 3.6*
2[p]	1.24	76	CS_2	16[t]	16.78	248	terthiophene
3[p]	1.95	84	thiophene	17[p]	17.02	256	S_8,
4[p]	3.48	98	3-methylthiophene	18[t]	17.41	262	monomethyl-terthiophene
5[p]	5.71	110	thiophene,ethyl	19[p]	18.06	248	2,2':5',2"-terthiophene
6[p]	9.72	134	benzo[b]thiophene	20[t]	18.35	248	terthiophene
7[p]	9.87	140	Thieno[3,2-b]thiophene	21[t]	18.77	262	monomethyl-terthiophene
8[t]	10.97	154	*see Figure 3.6*	22[t]	19.38	276	dimethyl-terthiophene
9[p]	11.76	166	2,2'-bithiophene	23[t]	21.63	330	tetrathiophene
10[p]	11.98	166	2,3' bithiophene	24[t]	22.20	344	monomethyl-tetrathiophene
11[t]	12.52	180	monomethyl-bithiophene	25[t]	22.68	358	dimethyl tetrathiophene
12[t]	12.75	180	monomethyl-bithiophene	26[p]	22.98	330	2,2':5',2":5",2"'-tetrathiophene
13[t]	13.25	198	*discussed in Section 5.2.2*	27[t]	23.63	344	monomethyl-tetrathiophene
14[t]	16.60	216	*see Figure 3.6*	28[t]	24.28	358	dimethyl-tetrathiophene

[p] Identified by matching its mass spectrum using mass spectral library or matching with standards;
[t] Tentatively identified by interpretation of mass spectra;
[s] Chemical structure of selected products are shown in Figure 3.6;
[m] Deduced from parent ion in its mass spectrum;
[r] As measured in pyrogram (Figure 3.5).

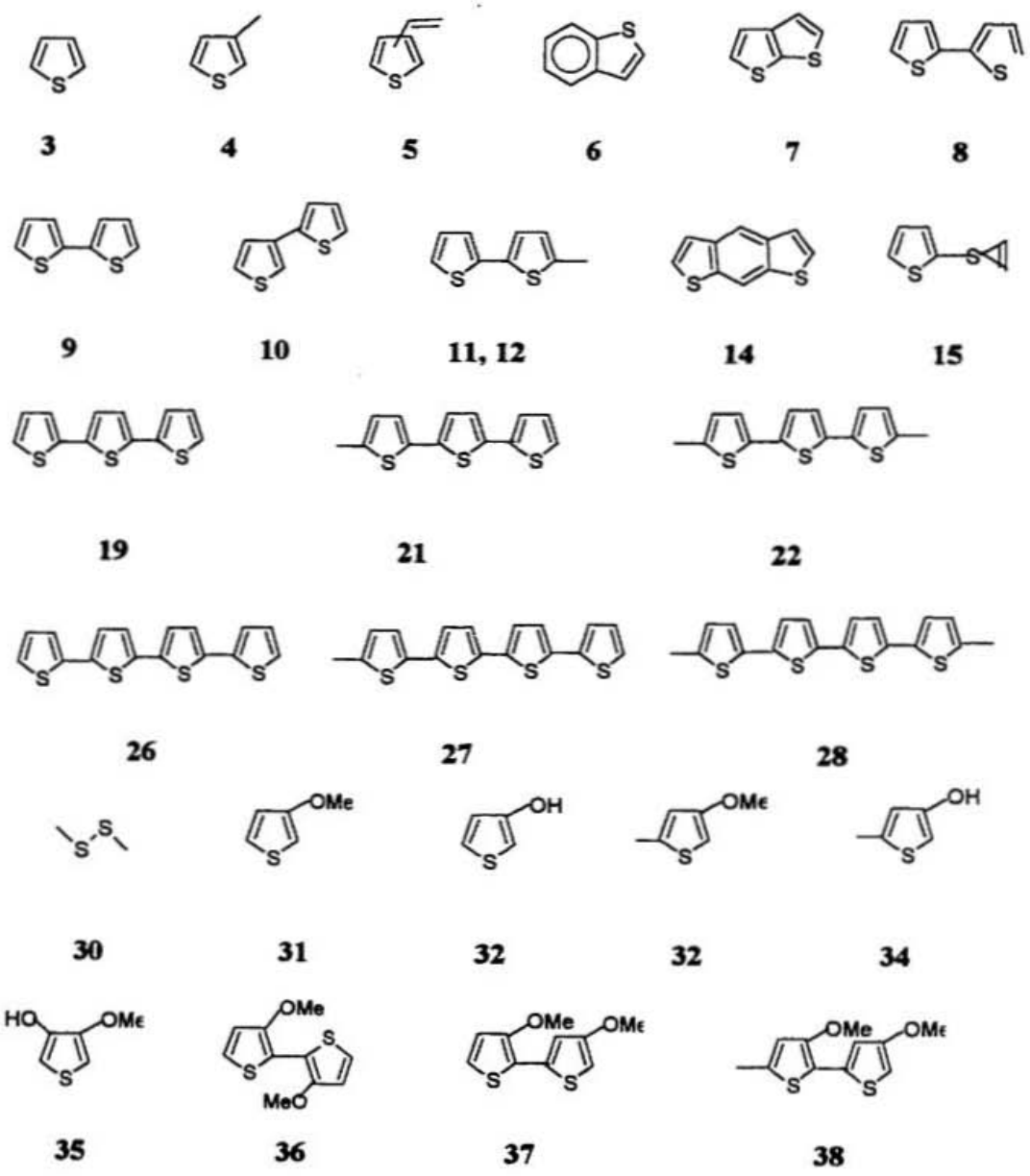


Figure 3.6 Chemical structures of pyrolytic products as listed in Tables 3.2-3.7. *Some structures are tentative denoted in tables.*

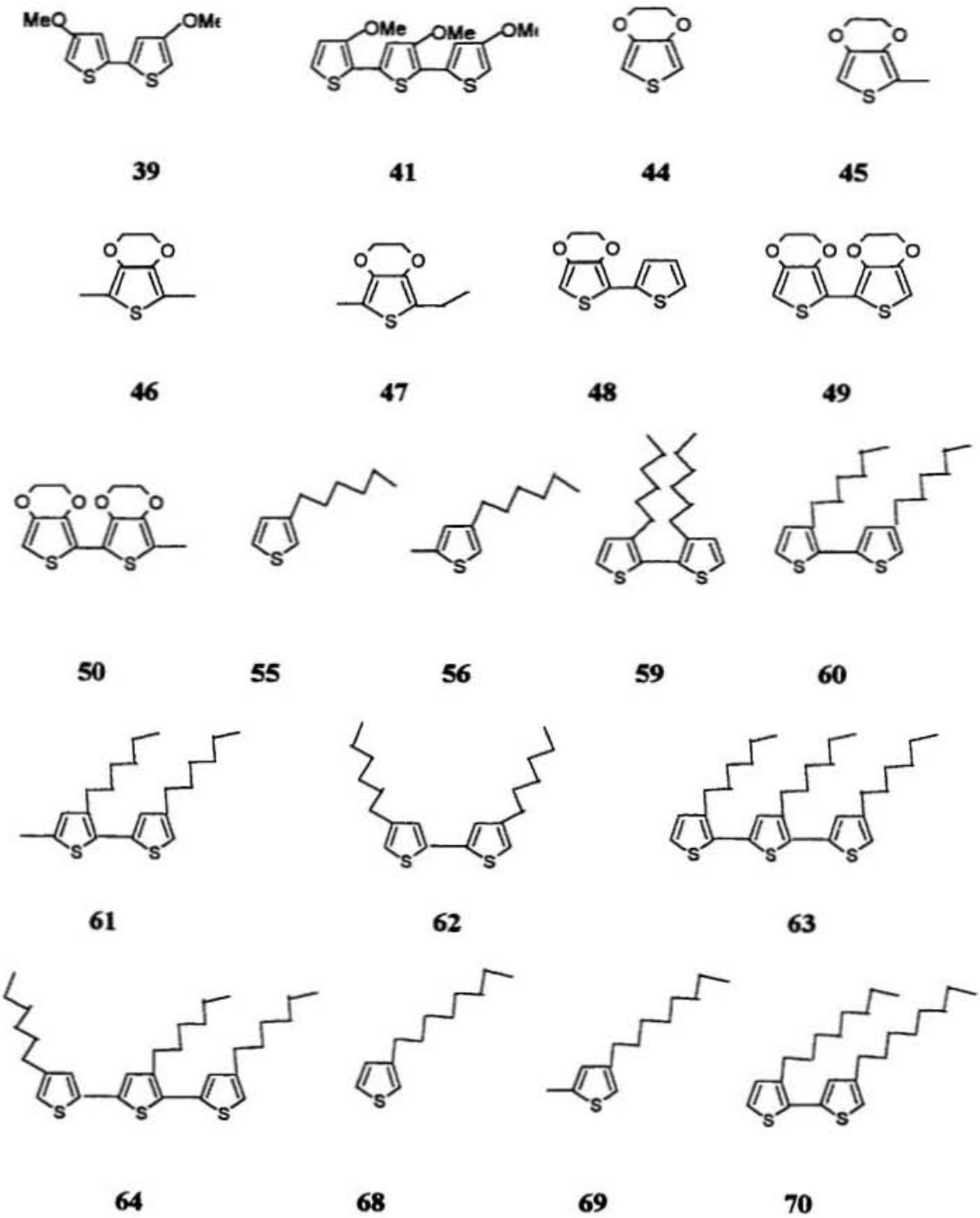


Figure 3.6 *... continued.*

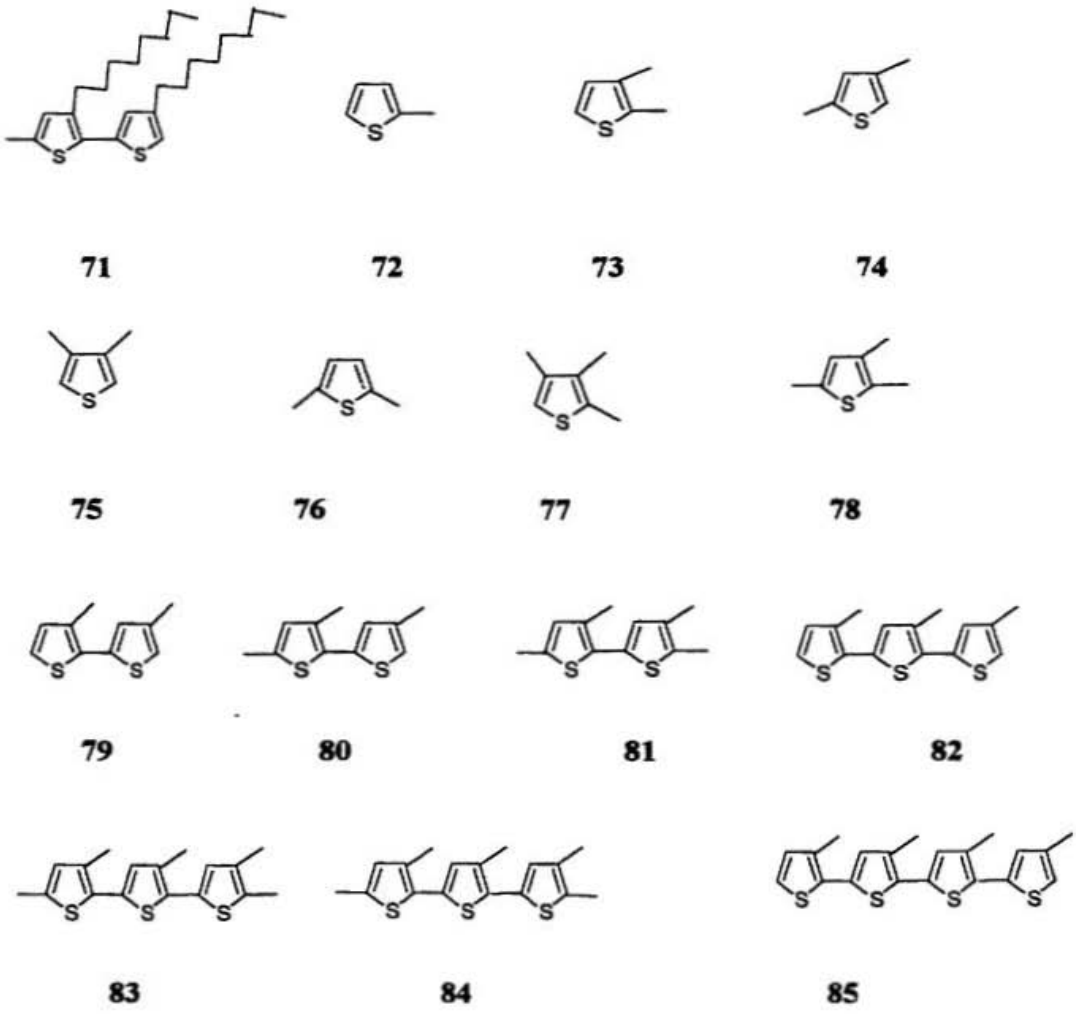


Figure 3.6 ... *continued*

EI mass spectra with those in the mass spectral library or by interpretation of their mass fragmentation pattern.

A large number of pyrolysates were identified. They can be divided into gases, one thiophene ring, two thiophene ring, three thiophene ring and four thiophene ring products. The gases are mainly H_2S, CS_2, CO_2 and SO_2. The oxygenated products are likely formed from trace amounts of oxygen in the carrier gas. The oligomer fragments principally consist of several isomeric oligomers and mono-and di-methyl oligomers. These characteristic fragments allow microstructure and bond cleavage information to be obtained as discussed in Chapter 5.

The distribution of the characteristic fragments are significantly different for PT, PBT and PTT (Figure 3.5). In the PT pyrogram, the major pyrolysates are a gas mixture (~84.5%; relative peak area), the oligomer fragments representing a much smaller fraction. The longer chain oligomers, such as tetrathiophene (**26**), could be barely observed. In contrast, in the pyrogram of PTT (Figure 3.5 (b)) the major products are oligomer fragments (~77.4%), such as tetrathiophene, terthiophene, bithiophene and their mono-methyl oligomers. For the PBT pyrolytic products, the yields of gases and higher oligomer pyrolysates are almost equal. From the results, it can be concluded that the increase in gases such as H_2S is at the expense of oligomeric fragment yields. An explanation for the pyrolytic behavior differences among the unsubstituted polythiophene is given Chapter 5.

3.4 Pyrolysis of Poly(3-methoxythiophene) and Poly(3,4-ethylenedioxythiophene)

Figure 3.7 shows a pyrogram of poly(3-methoxythiophene) pyrolyzed at 650°C. Table 3.3 lists the identified pyrolysis products and some of these structures are shown in Figure 3.6. Major pyrolysate include dimers (19.0% relative peak area), trimers (7.14%), and the monomer (30.9%), as well as methanethiol gas (23.8%). Minor pyrolysates include dimethyldisulfide and methylated oligomer fragments.

Figure 3.8 shows a pyrogram of poly(3,4-ethylenedioxythiophene) (PEDOT) pyrolyzed at 900°C. The identified peaks are listed in the Table 3.4 and selected structures are shown in Figure 3.6. In the pyrolysates, gas products (~ 85%) (e.g., ethene, carbon dioxide, and carbonyl sulfide), thiophene (0.48%), bithiophene (0.13%) and terthiophene (0.16%) were produced. Some products indicate the cleavage of $O\text{-}CH_2\text{-}CH_2\text{-}O$, the substituent on the thiophene ring. Thiophene ring cleavage also occurs as indicated by the presence of carbon disulfide and hydrogen sulfide. The monomer 3,4-ethylenedioxythiophene (**44**) and only one dimer (**49**) were observed, thus indicating that PEDOT is a true α-α' linked polymer. This result supplied useful information for the microstructure studies of various polythiophenes, discussed in detail in Chapter 5.

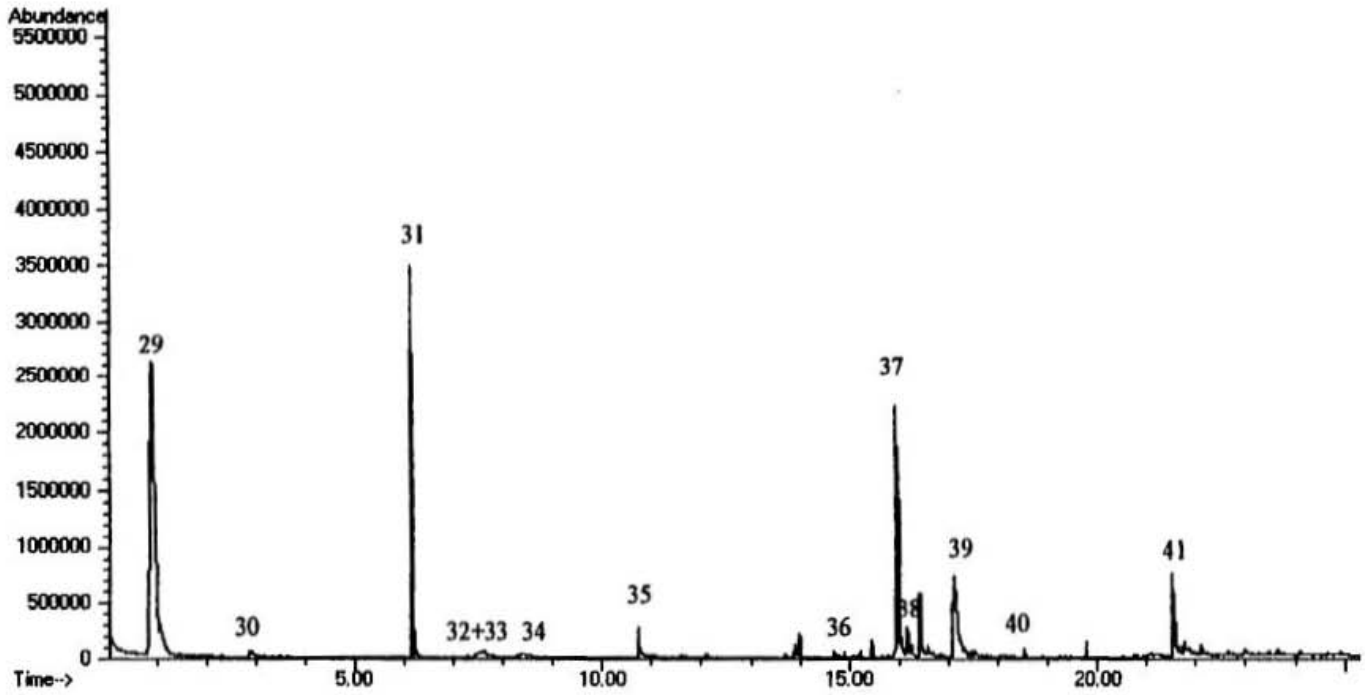


Figure 3.7 TIC pyrogram of poly(3-methoxythiophene) , T_{Py} = 650°C.
The identities of the numbered peaks are listed in Table 3.3.Ion abundances are measured in Scan mode.

Table 3.3 Identification of products in the pyrogram of poly(3-methoxythiophene)

No.	RT.[r]	M.W.[m]	Structure[s]	No.	RT.[r]	M.W.[m]	Structure[s]
29[p]	0.93	48	methanethiol	**36**[t]	15.45	226	3,3'-dimethoxy-2,2'-bithiophene
30[p]	2.88	94	dimethyldisulfide	**37**[t]	16.98	226	3,4'-dimethoxy-2,2'-bithiophene
31[p]	6.19	114	3-methoxythiophene	**38**[t]	16.25	240	monomethyl-3-methoxythiophene
32[t]	7.55	100	3-hydroxythiophene	**39**[t]	17.12	226	4,4'-dimethoxy-2,2'-bithiophene
33[t]	7.62	128	3-methoxy-5-methylthiophene	**40**[t]	17.48	242	?
34[t]	8.34	114	3-hydroxy-4-methoxythiophene	**41**[p]	21.58	338	3',4',4"-trimethoxy-2,2':5',2"-terthiophene
35[t]	10.74	130	3-methoxybithiophene				

[p] Identified by matching its mass spectrum using mass spectral library or matching with standards;
[t] Tentatively identified by interpretation of mass spectra;
[s] Chemical structure of selected products are shown in Figure 3.6;
[m] Deduced from parent ion in its mass spectrum;
[r] As measured in pyrogram (Figure 3.7).

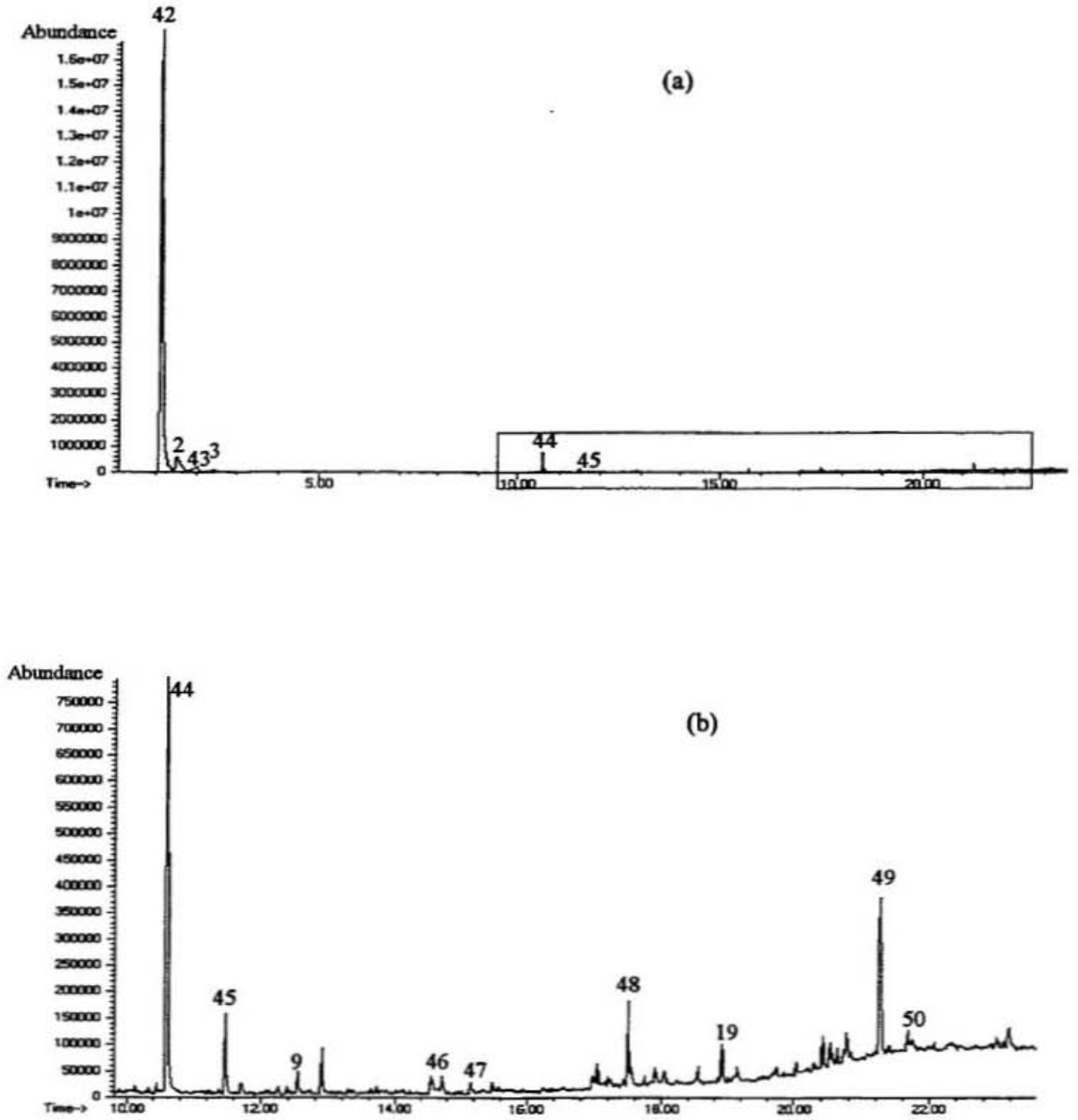


Figure 3.8 TIC Pyrograms of poly(3,4-ethylenedioxythiophene) (a) full pyrogram and (b) expanded region, $T_{py} = 900°C$.
The identities of the numbered peaks are listed in Table 3.4. Ion abundances are measured in Scan mode.

Table 3.4 Identification of products in the pyrogram of poly(3,4-ethylenedioxythiophene)

No.	R.T.[r]	M.W.[m]	Structure[s]	No.	R.T.[r]	M.W.[m]	Structure[s]
42[i]	1.12	28, 44	ethene, CO_2	**46**[p]	14.56	170	dimethyl-3,4-ethylenedioxythiophene
2[p]	1.52	76	CS_2	**47**[i]	15.17	184	*see Figure 3.6*
43[p]	2.04	60	acetic acid	**48**[i]	17.49	224	*see Figure 3.6*
3[p]	2.43	84	thiophene	**19**[p]	18.92	248	2,2':5',2"-terthiophene
44[p]	10.60	142	3,4-ethylenedioxythiophene	**49**[p]	21.26	282	dimer of peak **44**
45[p]	11.72	156	monomethyl-3,4-ethylenedioxythiophene	**50**[i]	21.68	296	monomethyl-dimer
9[p]	12.54	166	2,2'-bithiophene				

[p] Identified by matching its mass spectrum using mass spectral library or matching with standards;
[i] Tentatively identified by interpretation of mass spectra;
[s] Chemical structure of selected products are shown in Figure 3.6;
[m] Deduced from parent ion in its mass spectrum;
[r] As measured in pyrogram (Figure 3.8).

3.5 Pyrolysis Studies of Poly(3-alkylthiophene)s

In pyrolysis studies of poly(3-hexylthiophene) (Figure 3.9), identified products are listed in Table 3.5 and structures are shown in Figure 3.6. Major products were the hydrocarbons, 1-pentene and butane (37.7%) and hexane (7.28%). This indicates that the C_6 side chain on the thiophene ring was preferentially cleaved. Benzene (6.74%) may have originated from the reactions of alkene pyrolysates of the side chain. The presence of 3-hexylthiophene oligomer fragments shows that cleavage occurs between thiophene units and this reveals the structural repeat unit of the polymer.

The intensity of the major products varied with T_{py} from 600°C to 900°C. Benzene decreased and smaller volatile products, such as propene, appeared at the higher temperature (900°C) rather than butane which was a major main product for T_{py} below 800°C. This may be due to the fact that benzene is further decomposed at higher temperature. Also, when T_{py} is below 800 °C, 1-pentene was observed to be a major product. It is believed that whichever component is the main product depends on the stability of radicals produced during pyrolysis under different conditions.

In the pyrolysis study of poly(3-octylthiophene) (Figure 3.10) (Table 3.6), gases comprised ~ 91.5% of the pyrogram. Gases including propene (15.8%), hexane (27.4%), 1-heptene (39.3%) and octane (8.98%) indicating again that the C_8 side chain was cleaved

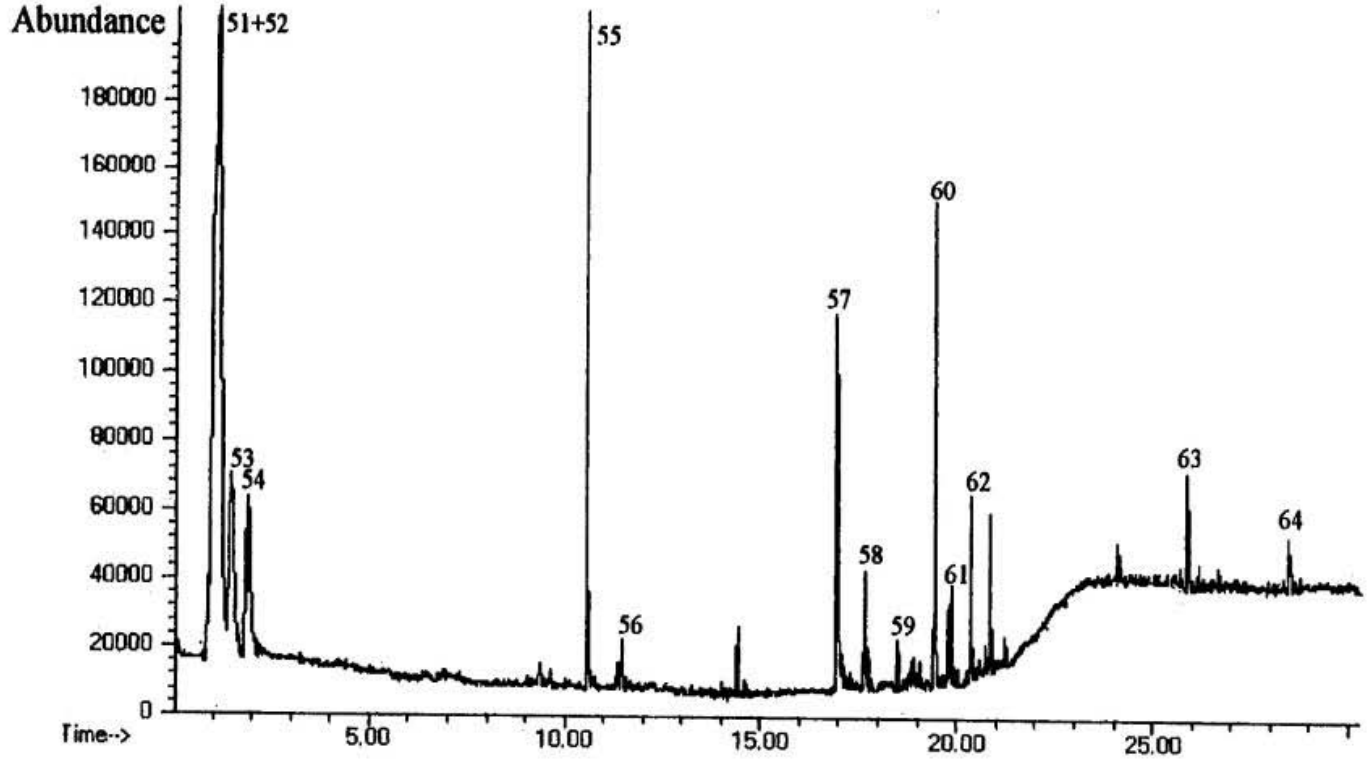


Figure 3.9 TIC pyrogram of poly(3-hexylthiophene), T_{py}= 600°C.
The identities of the numbered peaks are listed in Table 3.5. Ion abundances are measured in Scan mode.

Table 3.5 Identification of products in the pyrogram of poly(3-hexylthiophene)

No.	RT.[r]	M.W.[m]	structure[s]	NO.	RT.[r]	M.W.[m]	structure[s]
51[p]	1.02	58	butane	**58**	17.6	262	?
52[p]	1.03	70	1-pentene	**59**[p]	18.50	334	3,3'-dihexyl-2,2'-bithiophene
53[p]	1.47	86	hexane	**60**[p]	19.45	334	3,4'-dihexyl-2,2'-bithiophene
54[p]	1.89	98	benzene	**61**[t]	19.89	348	*see Figure 3.6*
55[p]	10.70	168	3-hexylthiophene	**62**[p]	20.37	334	4,4'-dihexythiophene-2,2'-bithiophene
56[t]	11.47	182	monomethyl-3-hexylthiophene	**63**[p]	25.89	500	3,4',4"-trihexyl-2,2':5',2"-terthiophene
57	16.95	228	?	**64**[p]	28.60	500	4,4',4"-trihexyl-2,2':5',2"-terthiophene

[p] Identified by matching its mass spectrum using mass spectral library or matching with standards;
[t] Tentatively identified by interpretation of mass spectra;
[s] Chemical structure of selected products are shown in Figure 3.6;
[m] Deduced from parent ion in its mass spectrum;
[r] As measured in pyrogram (Figure 3.9).

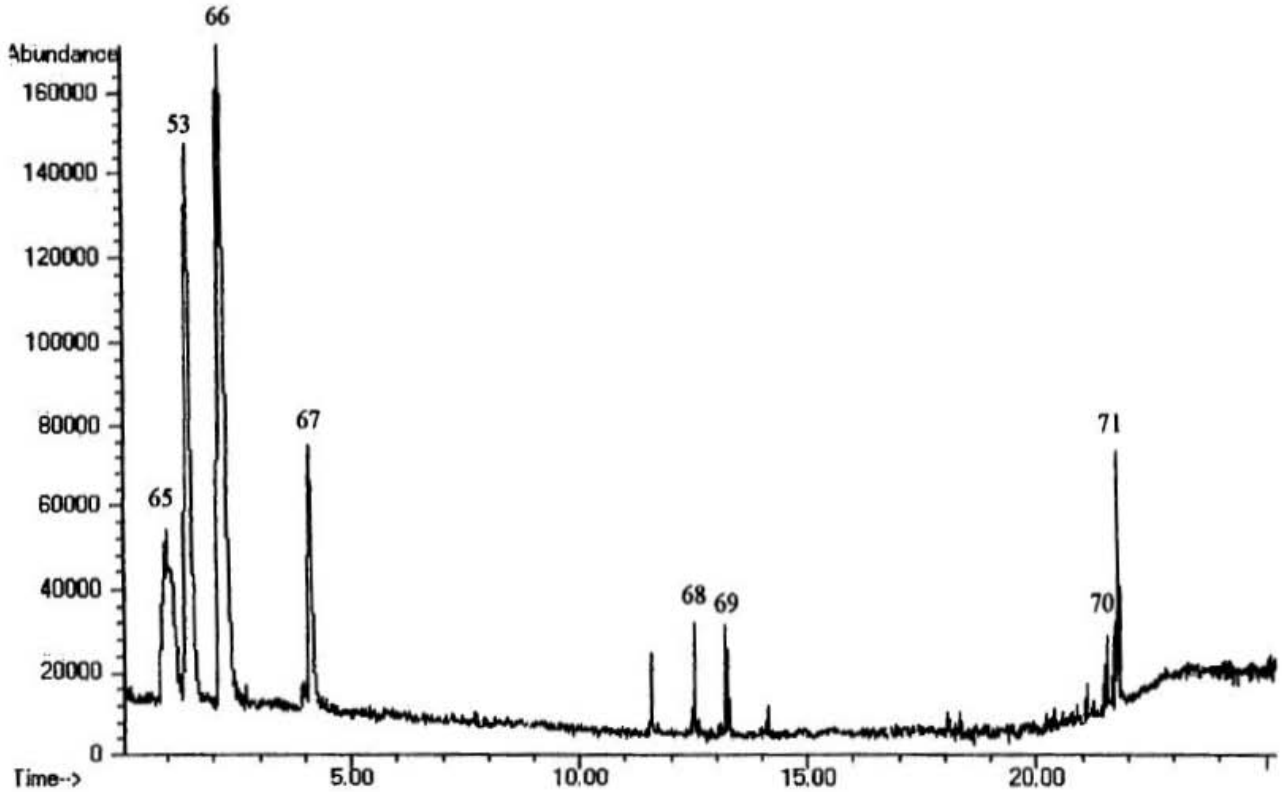


Figure 3.10 TIC pyrogram of poly(3-octylthiophene), T_{py} = 600°C.
The identities of the numbered peaks are listed in Table 3.6. Ion abundances are measured in Scan mode.

Table 3.6 Identification of products in the pyrogram of poly(3-octylthiophene)

No.	RT.[r]	M.W.[m]	structure[s]	No.	RT.[r]	M.W.[m]	structure[s]
65[p]	0.99	44	propane	**68**[p]	12.51	196	3-octylthiophene
53[p]	1.45	86	hexane	**69**[t]	13.24	210	monomethyl-3-octylthiophene
66[p]	2.17	98	1-heptene	**70**[p]	21.52	390	3,4'-dioctyl-2,2'-bithiophene
67[p]	4.12	114	octane	**71**[p]	21.84	404	dimethyl-dimer *(Figure 3.6)*

[p] Identified by matching its mass spectrum using mass spectral library or matching with standards;
[t] Tentatively identified by interpretation of mass spectra;
[s] Chemical structure of selected products are shown in Figure 3.6;
[m] Deduced from parent ion in its mass spectrum;
[r] As measured in pyrogram (Figure 3.10).

under pyrolysis. Also, some oligomers were formed, indicating the cleavage of the thiophene ring linkage. Similar to poly(3-hexylthiophene), as the pyrolysis temperature increased from 600 to 900 °C, the relative percentages of smaller pyrolysates, (i.e, propane and butane) increased.

In the case of the pyrolysis of poly(3-methylthiophene) (Figure 3.11), the nature of the prolysates is more complicated. They consist of thiophene, but also numerous isomers of methylthiophenes, dimeric, trimeric and tetrameric fragments, some of which are listed in Table 3.7. The production of H_2S indicates again that the thiophene ring can be broken, and the formation of unsubstituted thiophenes suggests that cleavage occurs between the methyl group and the thiophene ring.

3.6 Thermal Degradation Pathway of Poly(3-alkylthiophene)s Using Fractionated Pyrolysis

Fractionated pyrolysis is a technique which involves the analysis of the sample in stages at increasingly higher T_{py}. The same sample is pyrolyzed at different temperatures. This method can reveal how and at what temperatures different parts of the polymer thermally degrade [61]. For this experiment, samples of poly(3-hexylthiophene), poly(3-octylthiophene), or poly(3-methylthiohene), were pyrolyzed first at 700°C and then stepwise to 900°C.

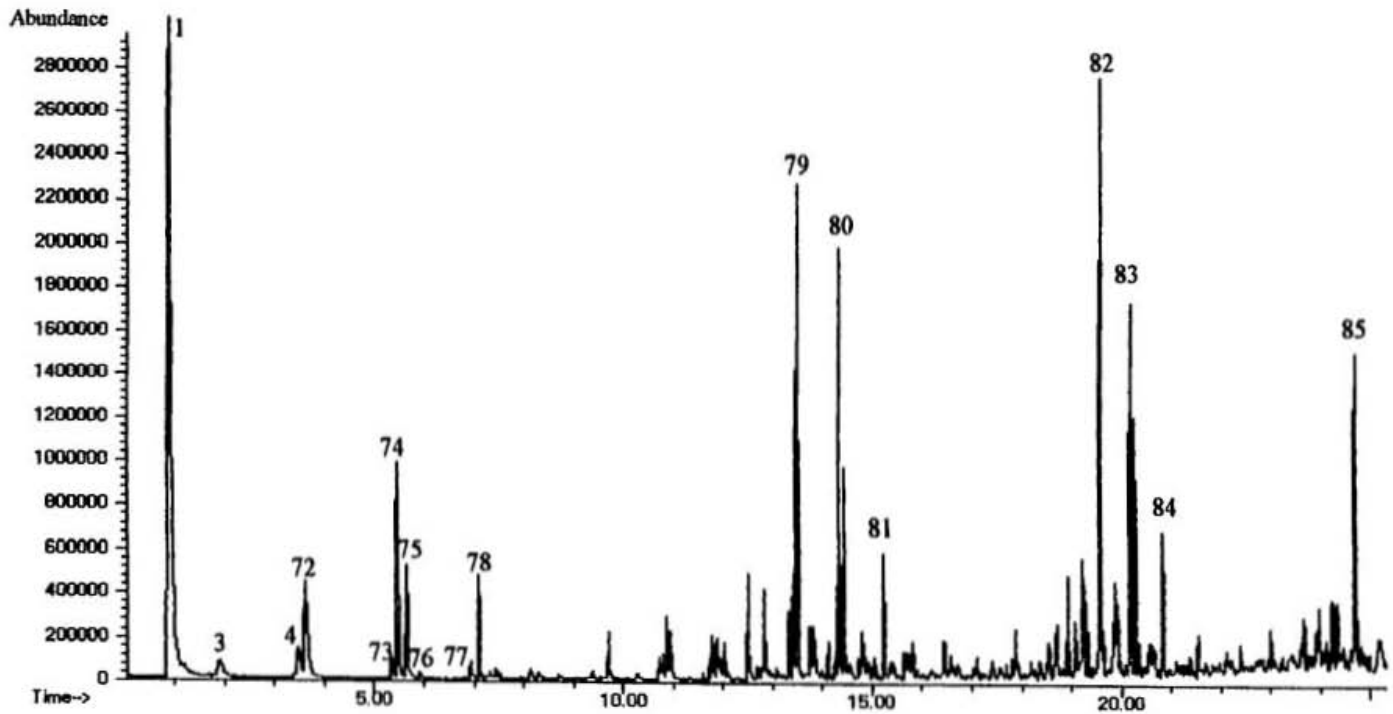


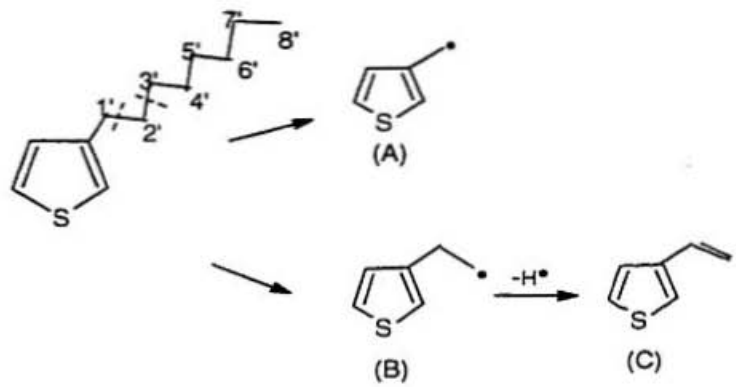
Figure 3.11 TIC pyrogram of poly(3-methylthiophene), T_{py} = 900°C.
The identities of the numbered peaks are listed in Table 3.7. Ion abundances are measured in Scan mode.

Table 3.7 Identification of products in the pyrogram of poly(3-methylthiophene)

No.	RT.[r]	M.W.[m]	Structure[s]	No.	RT.[r]	M.W.[m]	Structure[s]
1[p]	0.98	34	H_2S	**78**[t]	7.10	126	2,3,5-trimethylthiophene
3[p]	1.93	84	thiophene	**79**[t]	13.52	194	dimethyl-bithiophene
4[p]	3.49	98	3-methylthiophene	**80**[t]	14.34	208	monomethyl-bithiophene
72[p]	3.63	98	2-methylthiophene	**81**[t]	15.25	222	dimethyl-bithiophene
73[t]	5.35	112	2,3-dimethylthiophene	**82**[t]	19.67	390	3,4',4"-trimethyl-2,2':5',2"-terthiophene
74[t]	5.48	112	2,4-dimethylthiophene	**83**[t]	20.22	404	monomethyl-terthiophene
75[t]	5.66	112	3,4-dimethylthiophene	**84**[t]	20.83	418	dimethyl-terthiophene
76[t]	5.90	112	2,5-dimethylthiophene	**85**[t]	24.76	486	3,4',4",4"'-tetramethyl- 2,2':5',2":5"' tetrathiophene
77[t]	6.94	126	2,3,4-trimethylthiophene				

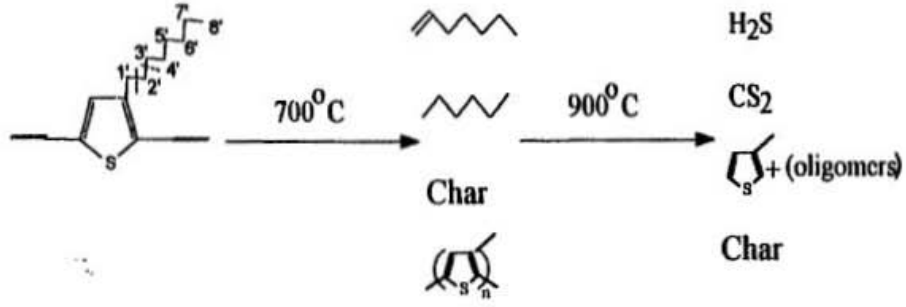
[p] Identified by matching its mass spectrum using mass spectral library or matching with standards;
[t] Tentatively identified by interpretation of mass spectra;
[s] Chemical structure of selected products are shown in Figure 3.6;
[m] Deduced from parent ion in its mass spectrum;
[r] As measured in pyrogram (Figure 3.11).

Figure 3.12 (a) illustrate the major products produced from the fractionated pyrolysis of poly(3-octylthiophene) (POT). At 700°C, a large amount of hexane and 1-heptene (gases) are formed and represent ~ 80% of the total pyrolysates. Their formation originates from cleavage of the C_8-side chain at C_1'-C_2' or C_2'-C_3'. When the residue is then pyrolyzed at 900°C, the thiophene rings are cleaved producing H_2S, while 3-methylthiophene and its oligomer fragments are formed from linkage cleavage. Similar results were obtained for fractionated pyrolysis of poly(3-hexylthiophene) (PHT).



The formation of butane and 1-pentene from C_6 side-chain cleavage, and hexane and 1-heptene from C_8 side-chain cleavage is consistent with the formation of radicals produced as indicated by structures A and B above. Generally, the more structural resonance the compound has, the more thermally stable it will be. Structure A is a π-stabilized radical with a number of resonance structures possible. Structure B is also a likely intermediate radical because it can form compound C which is structurally

(a)



(b)

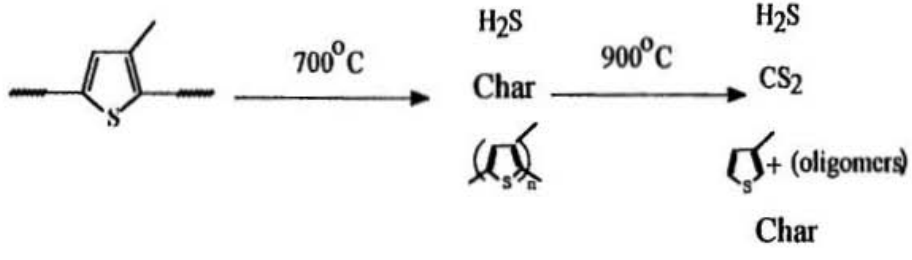


Figure 3.12 Major pyrolysis products when (a) poly(3-octylthiophene) and (b) poly(3-methylthiophene) are fractionally pyrolyzed at 700°C, then at 900°C

conjugated with the thiophene ring.

It was noted that the pyrogram of PHT at 900°C (after fractional pyrolysis at 700°C) is almost the same as that for POT. The original alkyl oligomer fragments can not be identified and both pyrograms are very similar to the pyrogram of poly(3-methylthiophene) pyrolyzed at 900°C. In contrast to fractional pyrolysis, pyrolysis of POT or PHT at a single T_{py} of 900°C did generate oligomers having the intact octyl or hexyl side chain.

Pyrolysis of poly(3-methylthiophene) at 700°C generated large amounts of H_2S gas and only small amounts of 3-methylthiophene oligomer fragments indicating ring cleavage at lower T_{py}. At high T_{py} 900°C, larger quantities of 3-methylthiophene oligomer thiophene ring pyrolysates were produced indicating that high T_{py} was required for linkage cleavage.

Chapter 4

Characterization of Unsubstituted Polythiophenes

4.1 Introduction

It is known that the electrical conductivity decreases from polythiophene (PT), to polybithiophene (PBT) to polyterthiophene (PTT) synthesized by electrochemical methods [12, 24]. The main reasons for this difference among unsubstituted polythiophenes are 1) the decrease in the average length of the conjugated π system and 2) increased incorporation of starting materials [12]. The limited conjugation length can be explained by the reactivity of the starting material. Its overall reactivity decreases as the length of the starting molecule increases. In other words, the stability of the corresponding radical cation (a reaction intermediate) increases with chain length, resulting in a decrease, and in some cases, a complete loss of polymerizability. This study will examine the pyrolytic behavior of PT, PBT and PTT and examine whether the results reflect the expected decrease in the length of conjugation. FTIR will also be used to confirm the decrease in conjugation length. It has been reported that PTT contains a large amount of unreacted terthiophene (TT) starting material and PBT contains some unreacted bithiophene (BT) after their electropolymerization [12, 24, 33]. In order to estimate the amounts of starting material

incorporated in the polymers, Py-GC-FID analysis were performed on PT, PBT, and PTT. However results showed that PT contained very little thiophene monomer. Calibration curves were constructed for FID responses of the starting oligomers.

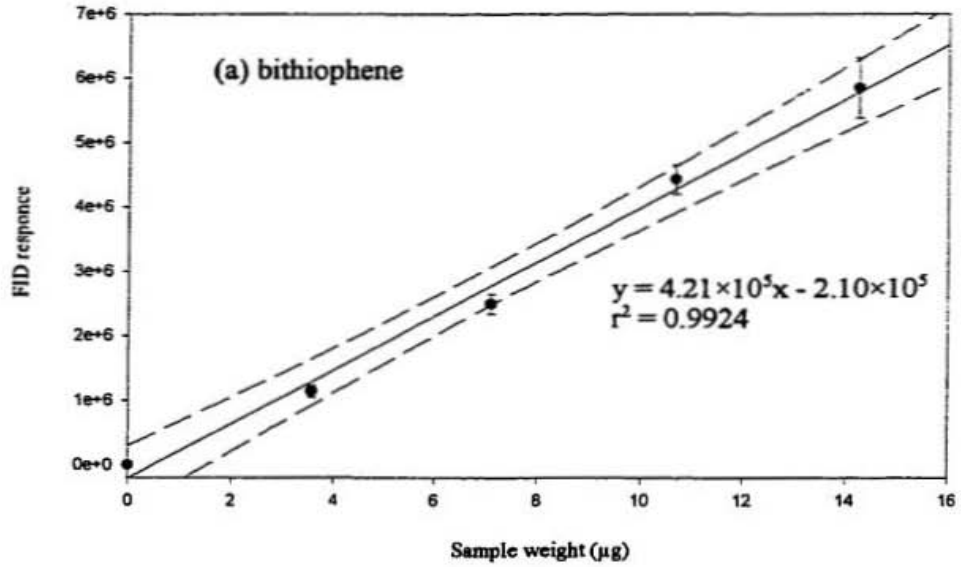
4.2 Analysis of Starting Material Incorporated into the Polymers

Both the analysis of polymeric samples and measurement of the detector response to oligomers were performed using the pyroprobe attached to the GC-FID as described in the experimental section. Chloroform solutions of BT (17.8 mg/10 ml) and TT(20.1 mg / 10 ml) were freshly prepared. Aliquots of 2, 4, 6 and 8 µl of each solution were analyzed by first injecting them into a quartz tube (with quartz wool), letting the chloroform evaporate (40 min) and finally thermally desorbing the oligomer using the pyroprobe. Calibration curves (with 95% confidence intervals) for BT and TT are shown in Figure 4.1. Linear fit equations were obtained as follows,

$$y = 4.21 \times 10^5 x - 2.10 \times 10^5 \qquad r^2 = 0.9924 \qquad \text{(for bithiophene)}$$

$$y = 5.28 \times 10^5 x + 4.10 \times 10^3 \qquad r^2 = 0.9998 \qquad \text{(for terthiophene)}$$

where x and y represents mass (µg) of the starting material and the FID response, respectively. Both correlation coefficients for calibration curves were satisfactory. The correlation coefficient for BT was found to be lower than that for TT, likely because of



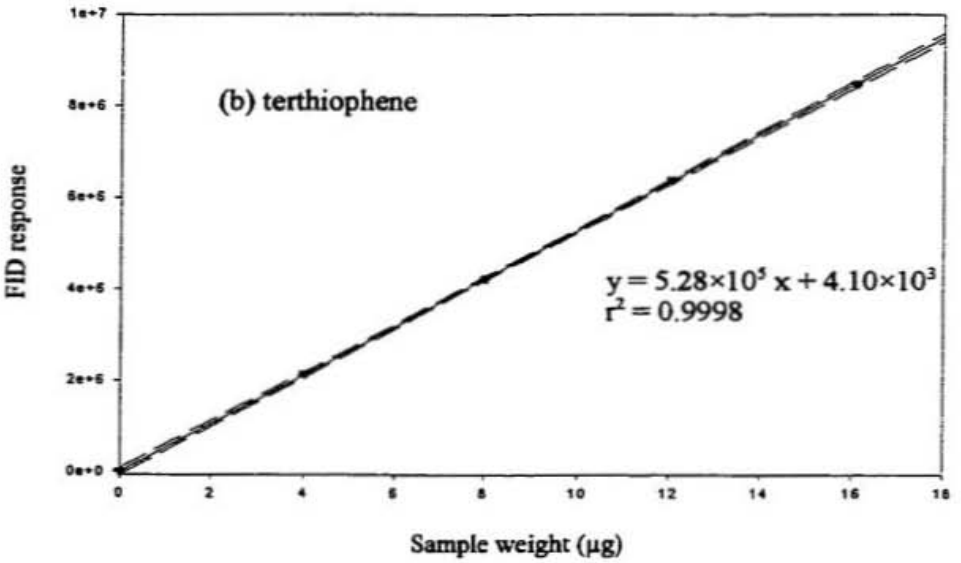


Figure 4.1 **Calibration curves for (a) bithiophene and (b) terthiophene.**
For each plot n =3. Points are means ± SD. Dashed lines represent 95% confidence interval.

BT's lower boiling point and the potential loss of material during solvent removal. Relative standard deviations are 7.0% for BT and 0.4% for TT. Poorer precision for BT again is likely due to its higher volatility.

From triplicate analyses each of PBT and PTT and using the calibration curves, it was calculated that PBT contains 3.8% ± 0.4 % BT starting material while PTT contained 6.2% ± 0.5% TT starting material. This is in agreement with prior reported qualitative estimation [12].

4.3 Comparison of IR Spectra

IR data of unsubstituted polythiophenes are listed in Table 4.1, including the C-H out-of -plane bending vibrations. The wavenumbers which are characteristic of the linkage positions, appear in the region 600-900 cm^{-1} [40]. The strongest band at around 786-790 cm^{-1} arises from 2,5-disubstituted thiophene rings. The corresponding bands in short-chain compounds, (i.e., terthiophene and tetrathiophene), lie at wavenumbers 7-12 cm^{-1} higher than those of the polymers [40]. Accordingly, the wavenumbers of this band are 784, 786 and 792 cm^{-1} for polythiophene, polybithiophene and polyterthiophene respectively. This band shift indicates that polythiophene has the longest conjugation length, while the conjugation length of polyterthiophene is the shortest.

The bands at 681-688 cm^{-1} arises from the 2 position of the-terminal thiophene (monosubstituted) that exists at the ends of a polymer chain [62]. Accordingly, the ratio

Table 4.1 Assignments of IR spectra of unsubstituted polythiophenes

unit: Wave number (cm^{-1})

Polyterthiophene	polybithiophene	polythiophene	polythiophene*	Bond
		3431	3421	C-OH
3065	3052		3093	C_β-H
	2925	2923	2922	C_β-H
		1661	1677	C=O
		1544	1524	C_α=C_β
1489	1487	1486		C_α=C_β
1427	1415		1415	C_α=C_β
	1330	1328	1369	C_β-C_β'
		1198	1211	C_α-C_α inter ring
	1117	1113		C_α-C_α inter ring
1067	1030	1029	1078	C_β-H
792	786	784	801	C_β-H out of plane
688	688	681		C_α-H at the terminal ring

**overoxidized polythiophene polymer*

of the intensity of this band versus that of the 784-792 cm^{-1} gives an approximation of the comparative degree of polymerization [40]. Ratios of 0.62, 0.23, 0.07 for PTT, PBT and PT respectively were calculated. Hence the degree of polymerization is the highest for PT and lowest for PTT.

The bands at 3431 cm^{-1} and 1661 cm^{-1} for PT indicates the presence of oxygen functional group and the topic of overoxidation will be discussed in Chapter 5.

4.4 Comparison of Pyrograms

As described in Chapter 3, pyrolysis products from PT, PBT and PTT are very similar. The pyrograms can be divided into five regions, that is, gas, one-thiophene-ring, two-thiophene-ring, three-thiophene-ring and four-thiophene-ring regions. However, the relative intensities of these pyrolysates are significantly different. The yields of the gas products decrease, while the yields of oligomer fragments increase in the order of PT to PBT to PTT.

In order to better understand this trend, selected ion monitoring (SIM) mode in GC-MS analysis was used. SIM refers to recording of the ion current at selected masses that are characteristic of the compound of interest. SIM pyrograms give excellent base line separation of chromatography peaks and satisfactory sensitivity.

Figure 4.2 shows SIM pyrograms of PT, PBT, and PTT, by monitoring m/z = 34 (H_2S), m/z = 76 (CS_2), m/z = 84 (thiophene), m/z = 98 (methylthiophene), m/z = 166 (bithiophene), m/z = 180 (methylbithiophenes), m/z = 248 (terthiophene), m/z = 262 (methylterthiophene), m/z = 330 (tetrathiophene) and m/z = 334 (methyltetrathiophene). These ions represent the major fragments characteristic of unsubstituted polythiophene from pyrolysis (Figure 3.5).

By taking the peak integrations of the SIM analysis, a comparison of relative yields of each pyrolysate region for PT, PBT and PTT was constructed (Figure 4.3). The results clearly show that the percentage of H_2S decreases from 62.6% (for PT) to 13.2% (for PTT), at the same time larger oligomer fragments such as trimers (i.e, terthiophene) and tetramers (i.e., tetrathiophene) increase significantly, (e.g., trimer yields from 2.1% (for PT) to 21.8% (for PTT).

These pyrolysis results reflect the fact that conjugation length decreases and/or the degree of polymerization of a polymer is reduced as the chain length of the starting oligomer increases from Th, BT to TT. With longer conjugation length the polythiophene polymer will likely break by thiophene ring thermal decomposition producing more gaseous products, such as H_2S and CS_2, and a smaller amount of oligomer fragments. This is due to the fact that longer conjugation enhances the bond strength between thiophene units. These result are in agreement with IR results described in Section 4.3.

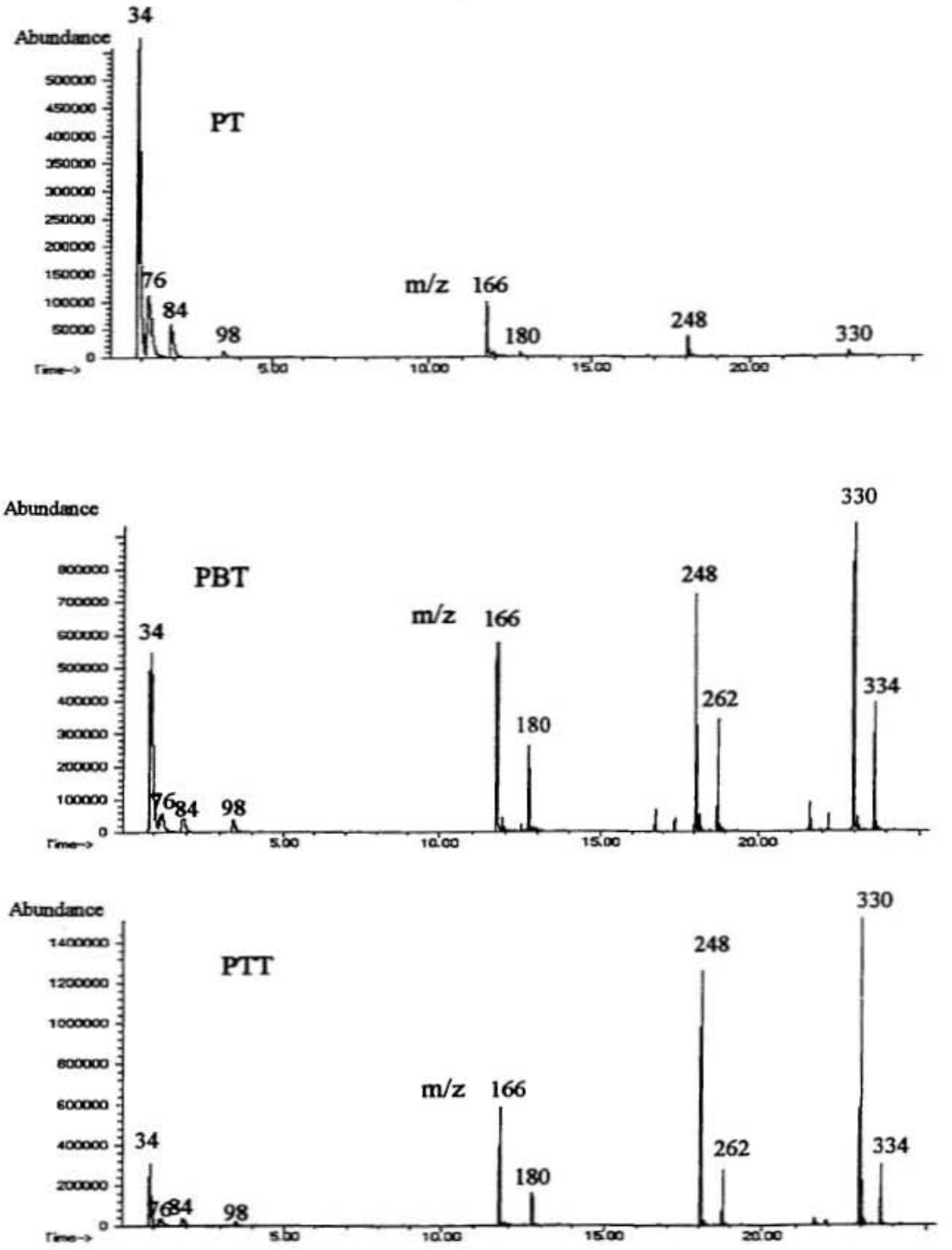


Figure 4.2 Pyrograms (T_{py} = 900°C) of PT, PBT and PTT using selected ion monitoring GC-MS. *The m/z numbered peaks correspond to key pyrolysis products are listed in Table 3.2.*

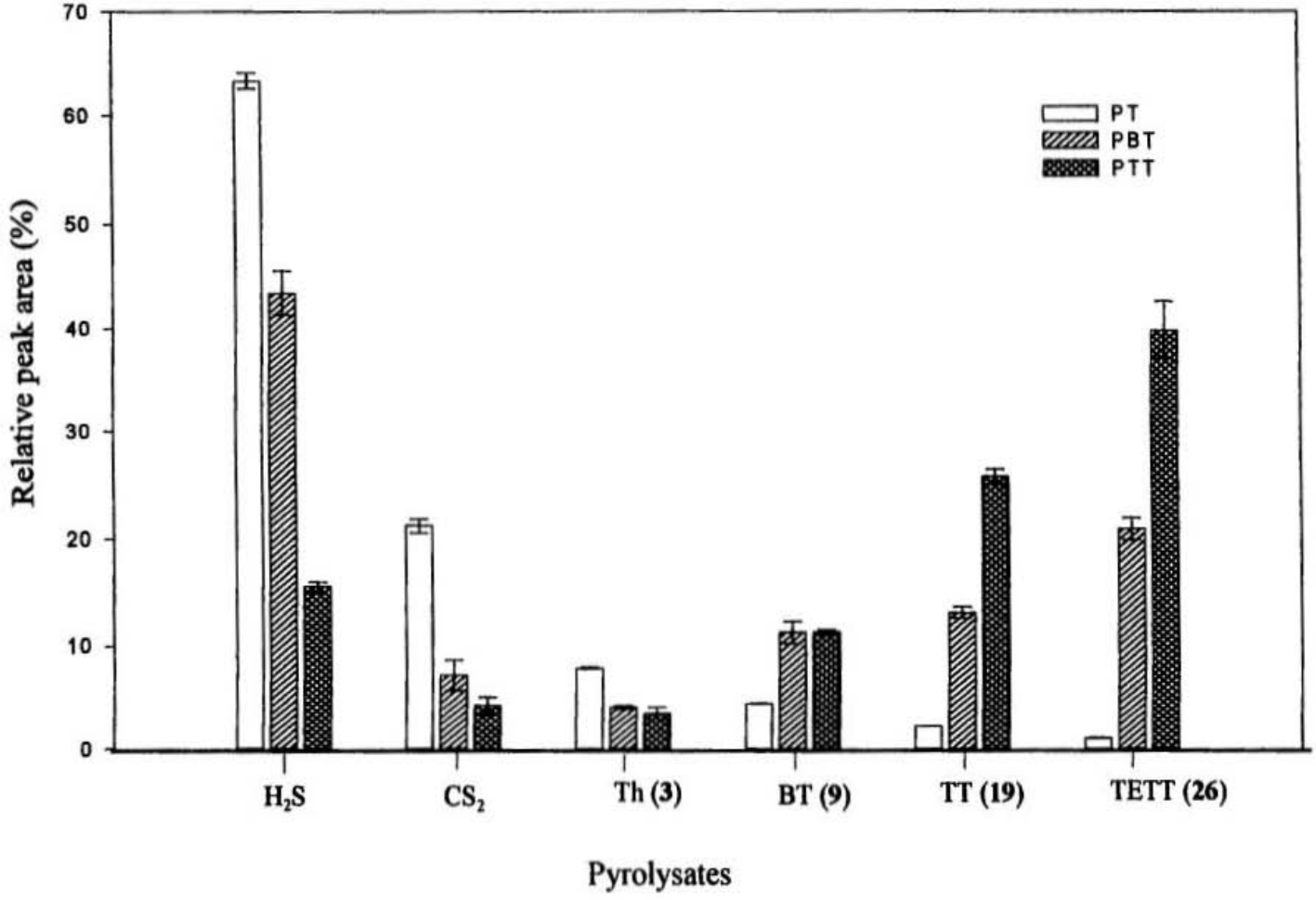


Figure 4.3 Comparison of yields of selected pyrolysates of PT, PBT and PTT using Py-GC-MS (SIM mode). *Error bars represent n = 3. The identities of the pyrolysates are listed in Table 3.2.*

The increased yields of higher oligomer fragments from PT, PB T to PTT may reflect the quality of the polymer. Good qualities of a conducting polymers are those with less α-β′ linkage, longer conjugation length and higher degree of polymerization. The α-β′ linkage is a weaker bond than α-α′ linkage and a higher percentage of α-β′ linkage in the polymer may result in higher yields of oligomer pyrolysates. A lower degree of polymerization also may result in a higher yield of oligomers because there is more effective oligomeric fragmentation at an increased number of end-groups.

4.5 Pyrolytic Behavior of Polythiophene Synthesized Successively

In order to further study the relationship between polymer quality and their pyrolytic behavior, successive polymerization experiments (described in Section 2.2.4) were conducted on PT and PBT. It was postulated that the relative intensities of pyrolytic oligomer fragments from polymers produced from the third successively polymerization should be higher compared with those from the first or second polymerized polymers. A polymer produced from the third repeated polymerization should have the poor quality because of the presence of increased amounts of α-β′-linkage.

Figure 4.4 illustrates the competitive reaction pathways during the electropolymerization of thiophene. In the first polymerization, there is only monomer, thiophene, as the starting material in solution. The reactivity of α and β positions of the

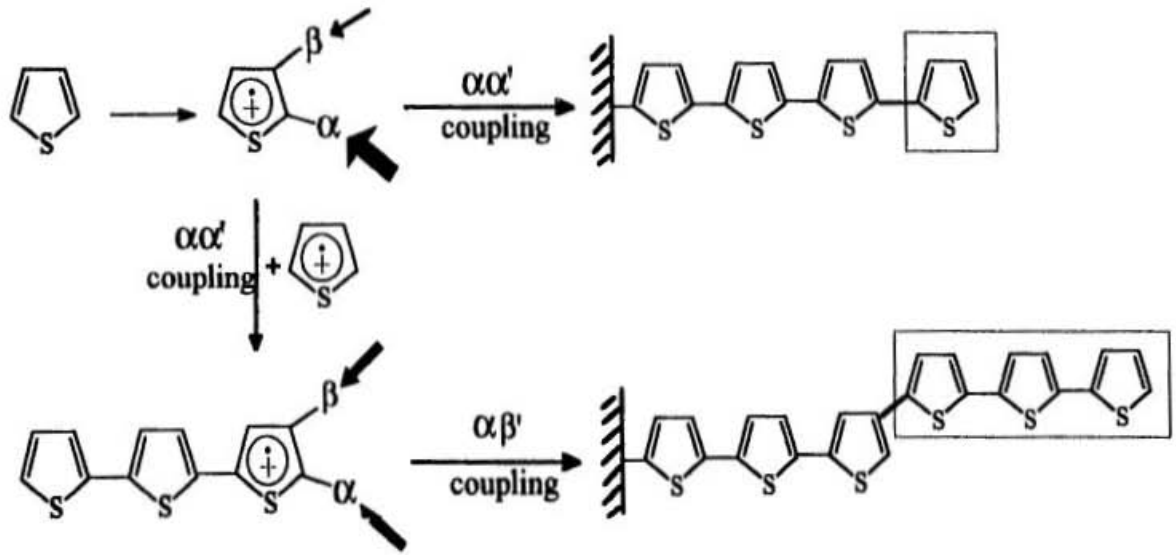


Figure 4.4 Competitive reaction pathways in the electropolymerization of thiophene

thiophene ring are significantly different. The α position is much more active than the β position and therefore most couplings will take place at the α position. In successively prepared polymers, besides the monomer thiophene, oligomers such as BT and TT formed during the first polymerization also exist in the solution [33]. The reactivity of the oligomers' α and β positions become progressively equivalent thus increasing the number of α-β′ couplings. This leads to a lower degree of conjugation in the polymer. Then the polymer produced from the third repeated polymerization from the same solution will have the poorest quality.

Figure 4.5 shows the pyrolysis yields of fragments from PT. It shows that the relative yields of oligomer fragments produced from the third polymerization are larger than those from the first polymerization. Similar results are obtained from the successive polymerization of PBT (Figure 4.6).

These results confirm the postulation about the relationship between polymer quality and pyrolytic behavior. That is, a poor quality polymer, one which contains more α-β′ linkages, (shorter conjugation length) will produce higher yields of oligomer fragments upon pyrolysis because of the weaker α-β′ linkage.

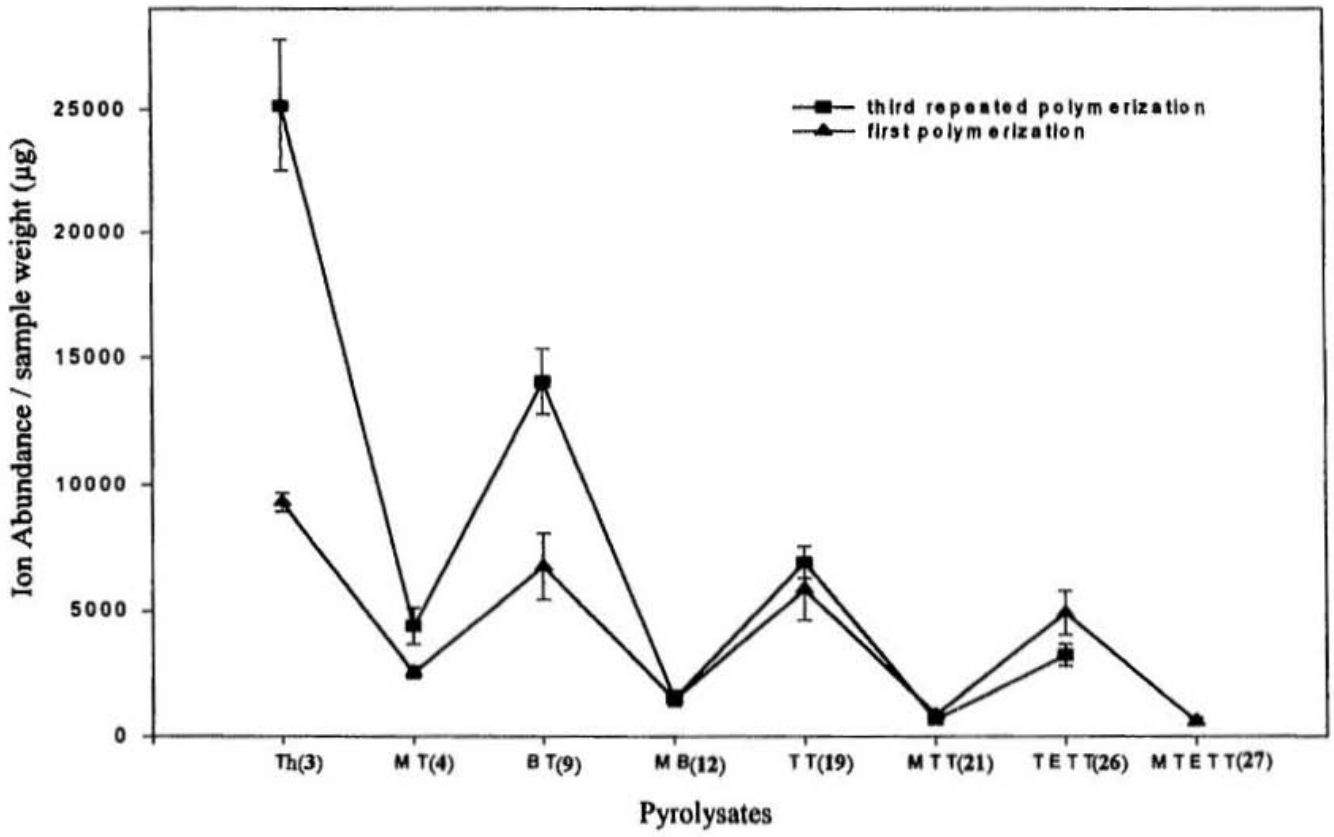


Figure 4.5 Pyrolytic yields from polythiophene produced from successive electropolymerization. *The identities of the pyrolysates are listed in Table 3.2. Error bars repeat n = 3.*

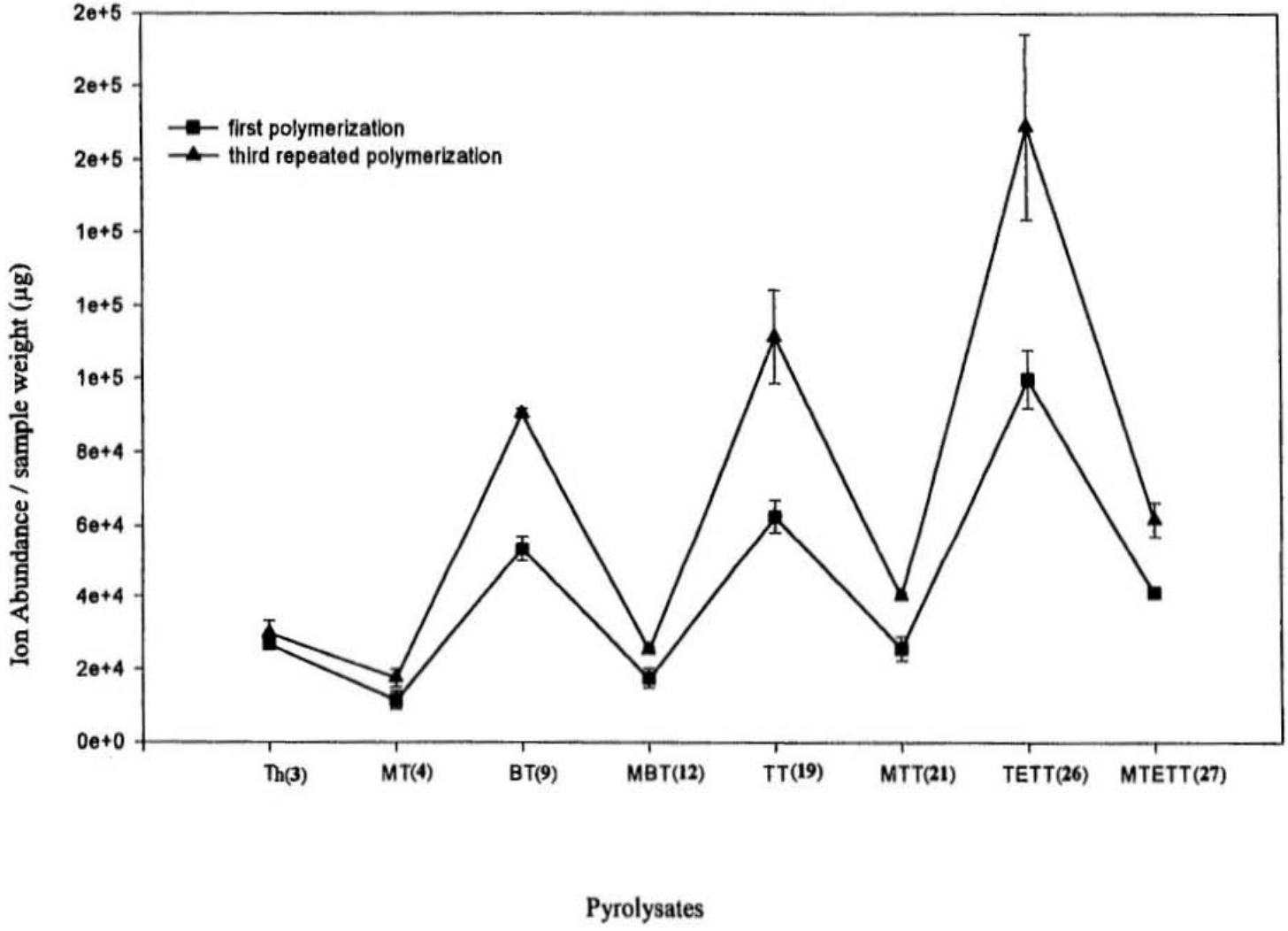


Figure 4.6 Pyrolytic yields from polybithiophenes produced from succesive electropolymerization. *The identities of the pyrolysates are listed in Table 3.2. Error bars repeat n = 3.*

Chapter 5

Microstructure Studies

5.1 Introduction

The properties (e.g., apparent color, conductivity) of conducting polymers are largely dependent on the mean effective conjugation length along the polymer chain. The mean effective conjugation length is determined by two parameters. One is the ratio of the defected linkage, α-β′, to conjugated linkage, α-α′,(refer to section 5.2.1) and the other is the planarity of the extended π conjugation system [12].

It has been reported that electrochemically-generated unsubstituted polythiophene, (i.e., polythiophene synthesized from thiophene) have non-negligible α-β′ defect coupling besides the dominant α-α′ conjugated linkage [20]. Santos and Bredas reported the role of α-β′ linkages in the electronic structure of polythiophene chains, in particular their influence on the conjugation length (delocalization) of the upper occupied valence states [66].

In 3-substituted polythiophenes (i.e., poly(3-alkylthiophene)s and poly(3-alkoxythiophene)s), introducing a group at the β position is expected to reduce or

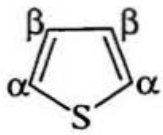
eliminate α-β′ coupling, thus favoring a longer effective conjugation length. However, head to head (HH) or tail to tail (TT) configurations in 3-substituted polythiophene will create steric hindrance between thiophene units and this will have a negative effect on the effective conjugation length.

HH coupling present in a HT-HH example of a tetramer, dramatically alters the conformation of the molecule. The thiophene rings at the HH junction maintain a trans conformation, but are twisted approximately 40° from coplanarity [42]. This is an important point because it has been reported that the π electron orbital must be within 30° of coplanarity in order to achieve enough overlap to generate conducting polymer band structure [63]. Calculations indicate that HH (or TT) couplings along the polythiophene chain destroy conjugation by inhibiting intrachain charge mobility [64]. In contrast, HT coupling as in a HT-HT tetramer prefer a trans-coplanar orientation where adjacent thiophene rings are twisted by only 20° [65].

In this study, we attempt to investigate linkage features of thiophene-based polymers by the analysis of the structures of oligomeric fragments generated from pyrolysis of the polymers.

5.2 Unsubstituted Polythiophenes

5.2.1 α-α′ and α-β′ Coupling



For linkage notation an α carbon is adjacent to the sulfur atom (i.e., positions 2 and 5). Similarly a β carbon is the 2th carbon from the sulfur (i.e., positions 3 and 4). An α-α′ bond is denoted as a bond between an α carbon of the first ring and an α′ carbon of the second ring. For larger oligomers the same notation is employed to distinguish various forms as long as one restrict ourselves to linear chains.

The electrochemically-synthesized unsubstituted polythiophenes, (PT, PBT and PTT) were analyzed by Py-GC-MS in order to identify the presence of oligomeric fragments containing α-β′ linkages. Selected ion monitoring MS was used as an effective way of searching for such fragments. The ions m/z = 84, 166, 248, and 330, were monitored representing the molecular ions of thiophene, bithiophenes, terthiophenes and tetrathiophenes, respectively. Figure 5.1 shows the SIM pyrogram of oligomers produced from the pyrolysis of PBT. One monomer, two dimers, three trimers, and four tetramers were observed. The two dimers have similar mass spectra as shown in Figure 5.2. This is also the case for the trimers and tetramers. This indicates that the dimers, the trimers and

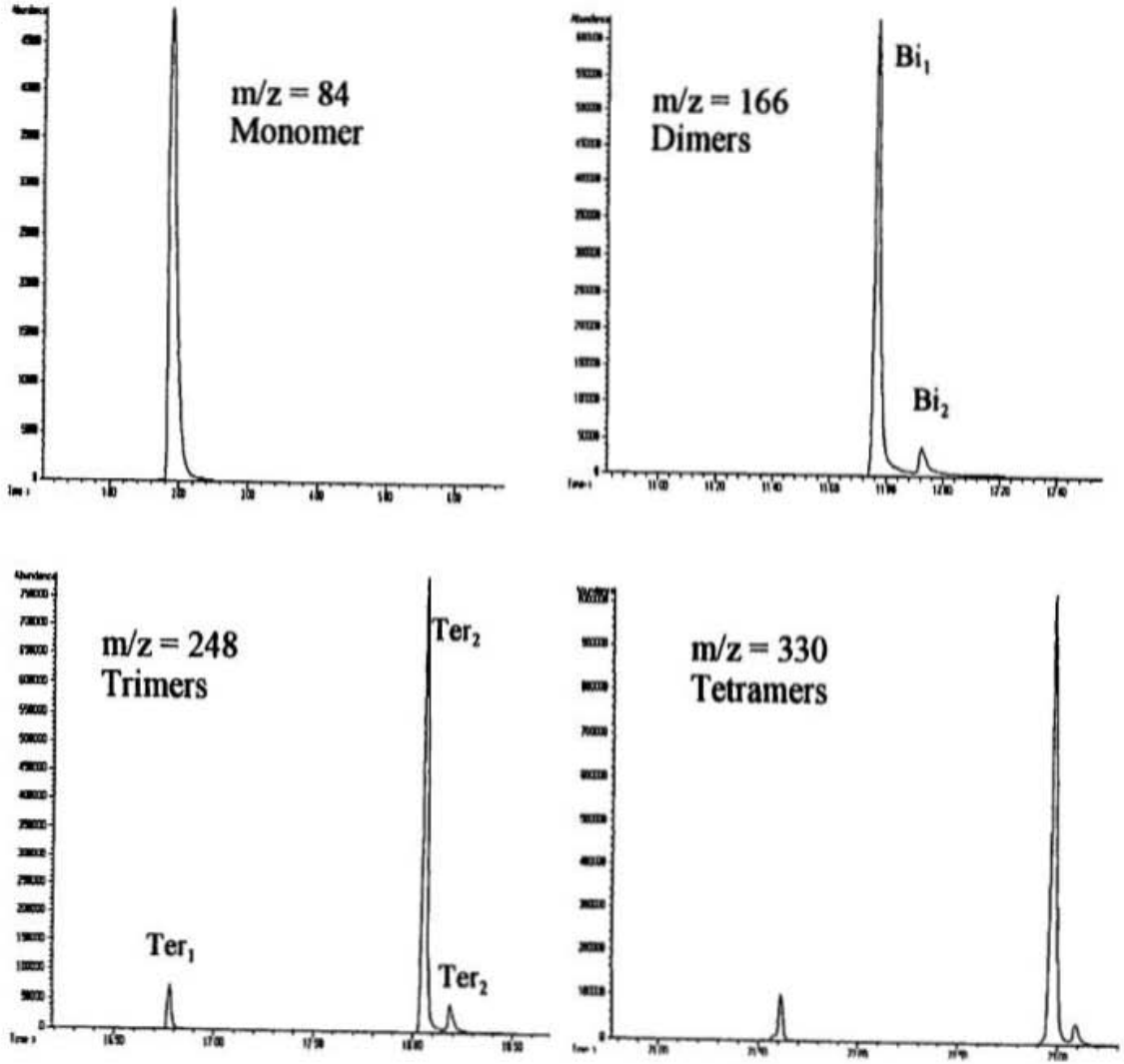


Figure 5.1 SIM pyrograms (T_{py} = 900°C) of oligomers produced from the pyrolysis of PBT. *The identities of the labelled peaks are shown in Figure 5.4.*

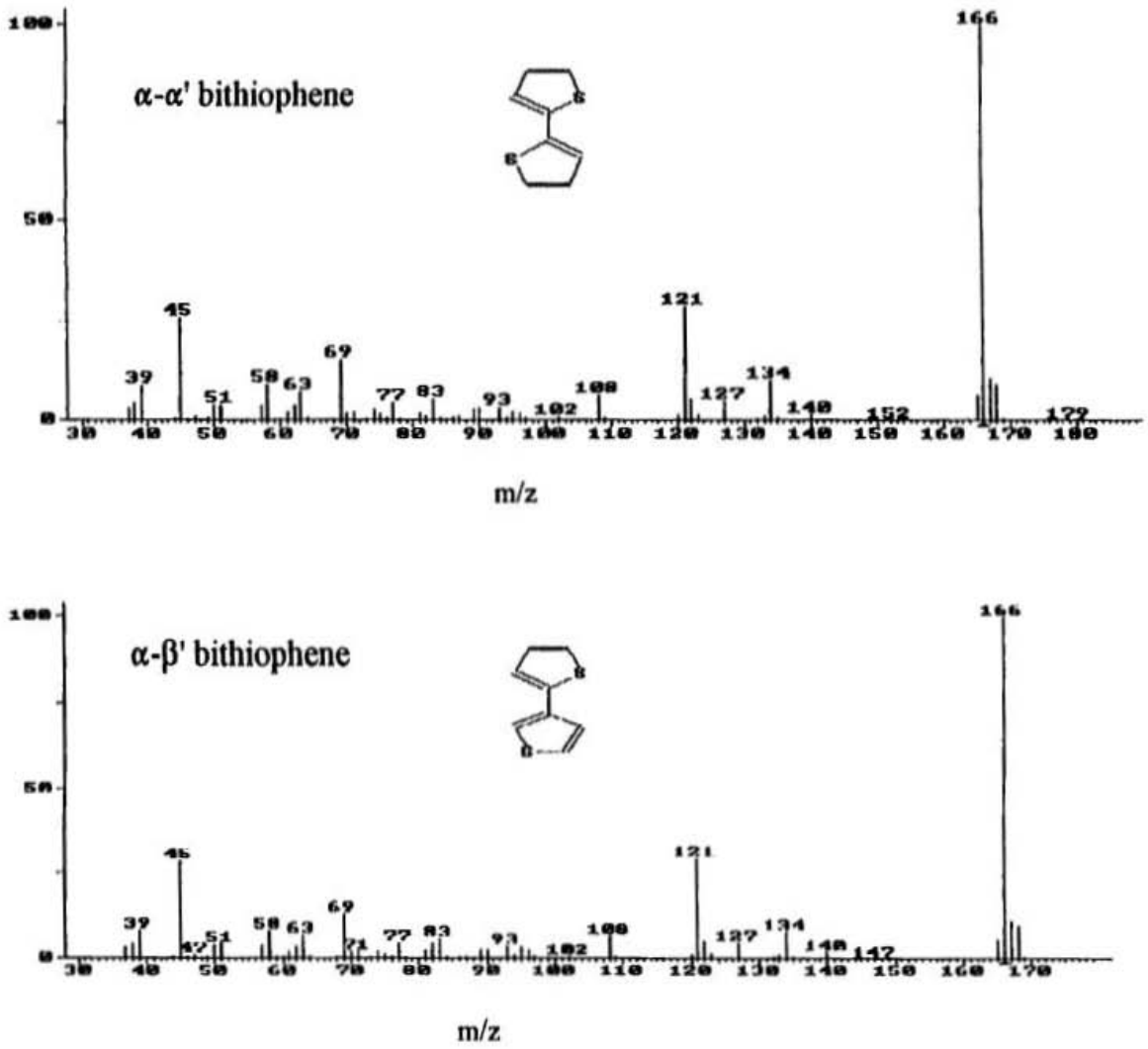


Figure 5.2 Mass spectra of bithiophene products from the pyrolysis of polythiophenes.

four tetramers represent groups of isomers.

Although the exact structures of the isomers can not be determined by MS, they elute at different retention times on the analytical column, depending on their boiling points or molecular polarity. Some of the isomers can be identified by comparing their retention time to that of the oligomer standards with pure α-α′ couplings and possibly by empirical polarity calculations. β-β′ linked thiophene oligomers were not considered due to their low probability of formation.

The α-α′ linked oligomers can be identified by comparing the SIM pyrogram of PBT to the total ion chromatogram of α-α′ coupled thiophene oligomer standards (Figure 5.3). The most intense peak in every isomer group is thus identified as to the α-α′ coupled thiophene oligomer. The smaller chromatographic peaks should be α-β′ linked isomers. In the case of the dimer isomers the peak at 11.76 min is ascribed to α-α′ -bithiophene, and that at 11.98 min, α-β′ -bithiophene (see figure 5.1). This result is in agreement with their expected molecular polarity. Consideration of the geometric symmetry of the two dimers would indicate that α-α′ bithiophene is more symmetric (less polar) and would have the shorter retention time. This was confirmed empirically by polarity calculations using a semi-empirical / AM1, geometry optimization using the Spartan program. The calculated dipole moment values are 0.000 debye and 0.059 debye for α-α′ bithiophene and α-β′ bithiophene, respectively.

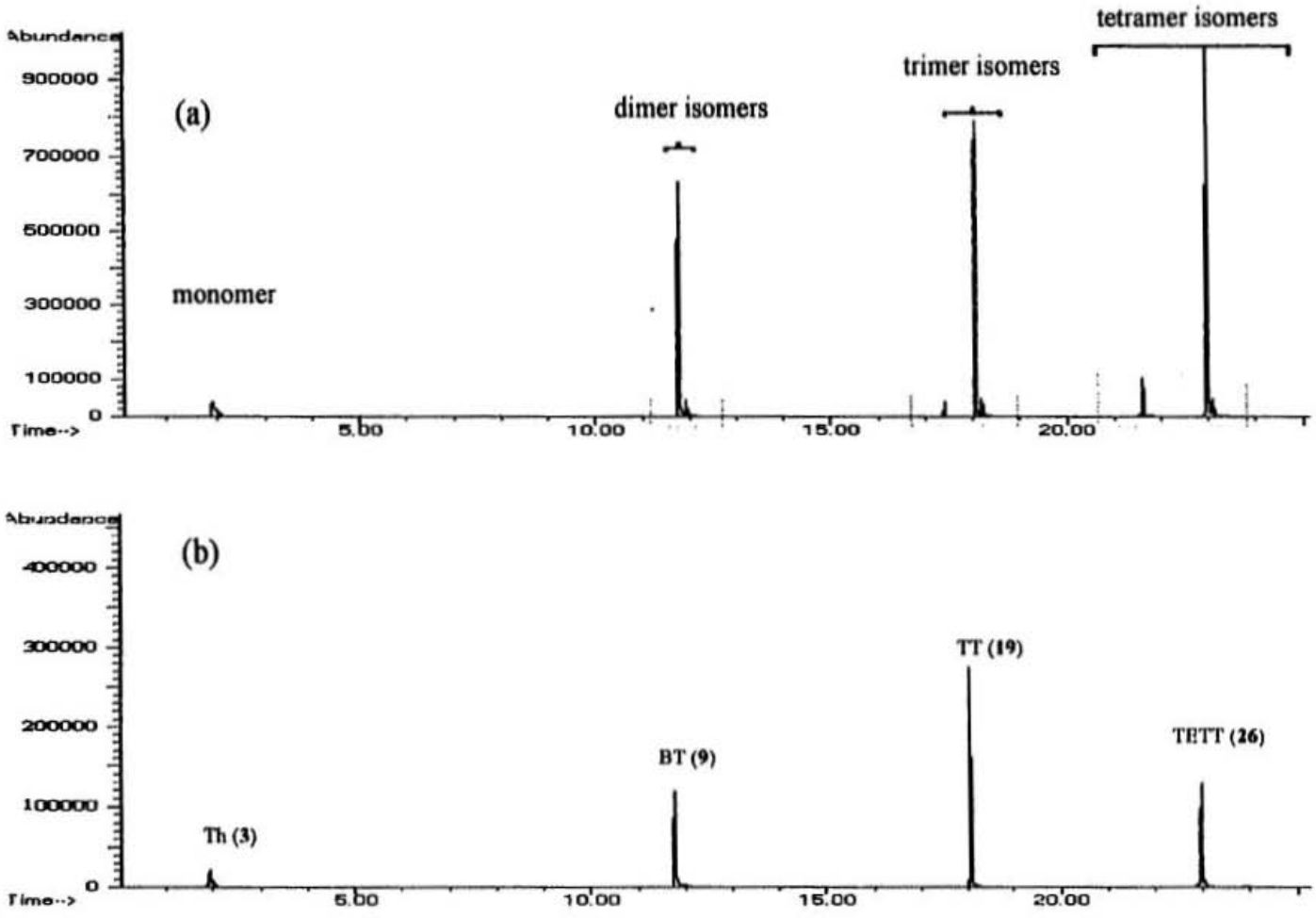


Figure 5.3 (a) Pyrogram of thiophene oligomers produced from PBT. (b) TIC of α-α′ coupled thiophene oligomer standards. *Dashed regions in (a) are those shown in Figure 5.1.*

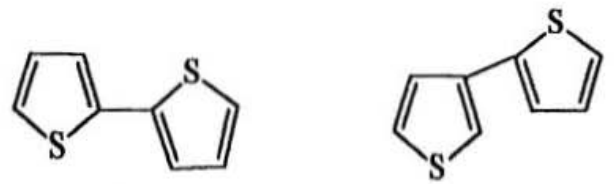
The chemical structures of the dimer and trimer isomers labeled in Figure 5.1, 5.5 and 5.6 are shown in Figure 5.4. The above analysis was also applied to PT and PTT. Similar results were obtained, (i.e., two dimer, three trimer and four tetramer pyrolysis products having identical retention times (Figure 5.5 and Figure 5.6).

The presence of significant α-β′ couplings in unsubstituted PTs is further supported from the pyrolytic analysis of PEDOT. PEDOT was chosen as the reference compound because the two β positions of its monomer are occupied by the ethylenedioxy group. Only the α position is available for coupling when it is polymerized. Therefore, PEDOT should be exclusively an α-α′ coupled polymer. Only one dimer was obtained in its pyrogram as expected (Figure 3.8).

In conclusion, the existence of significant amounts of α-β′ linked-oligomers in the pyrolysates afford strong evidence that α-β′ linkage do exist in polythiophenes. It is expected that analytical pyrolysis will be a useful method in determining the extent of α-β′ -linkages in commercial products in the future.

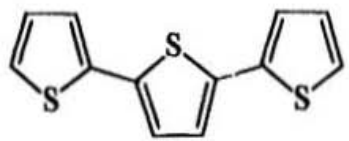
5.2.2 Overoxidation of Polythiophene

The term "overoxidation" refers to the chemical degradation of a electrochemically

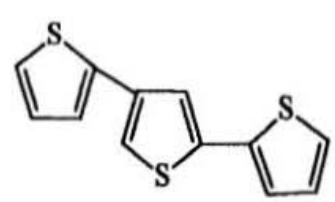


Bi_1

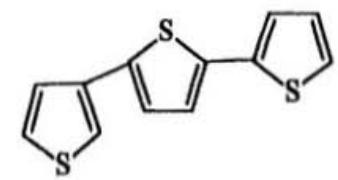
Bi_2



Ter_2



Ter_1 or Ter_3



Ter_1 or Ter_3

Figure 5.4 Chemical structures of dimer and trimer isomers identified in the pyrolysis of polythiophenes.

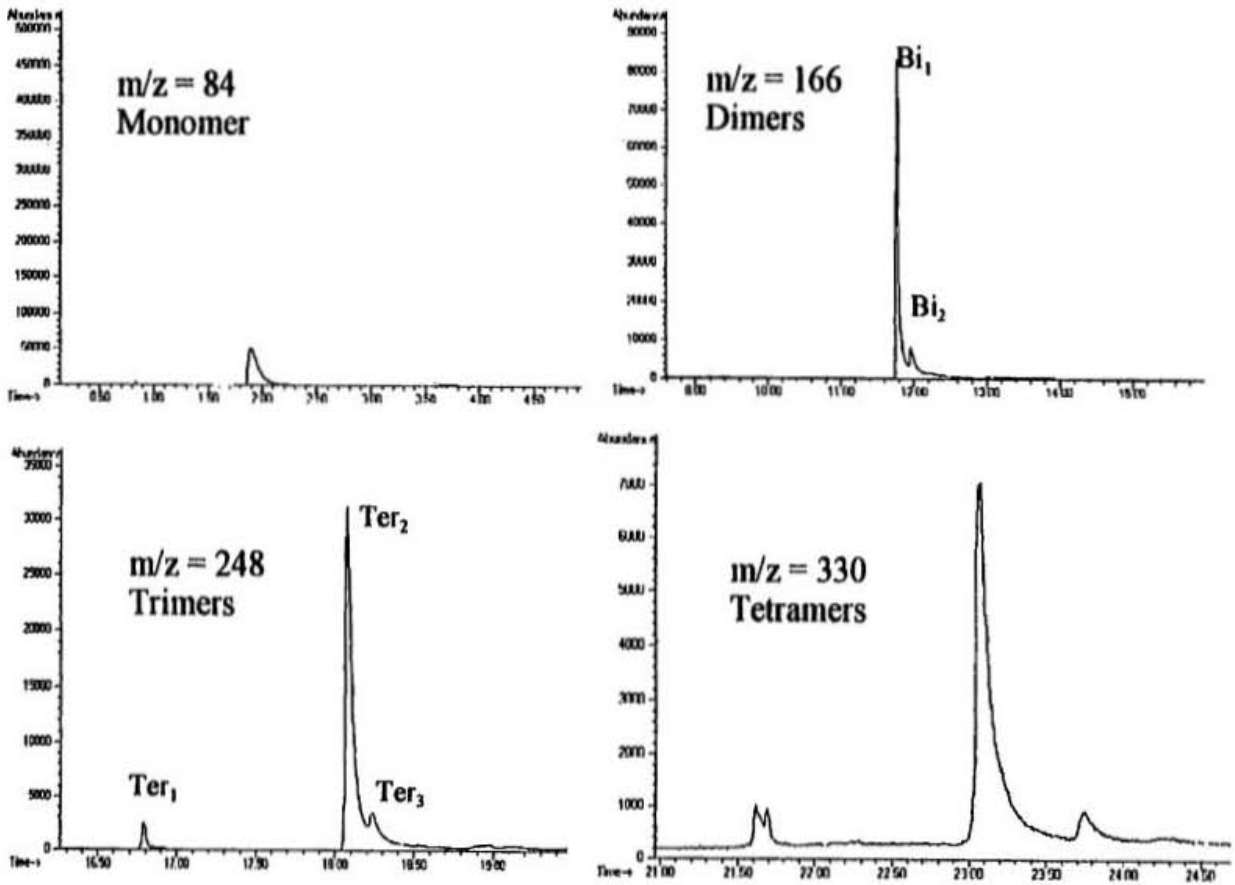


Figure 5.5 SIM pyrogram (T_{py} = 900°C) of oligomers produced from pyrolysis of PT. *Identities of the labeled peaks are shown in Figure 5.4.*

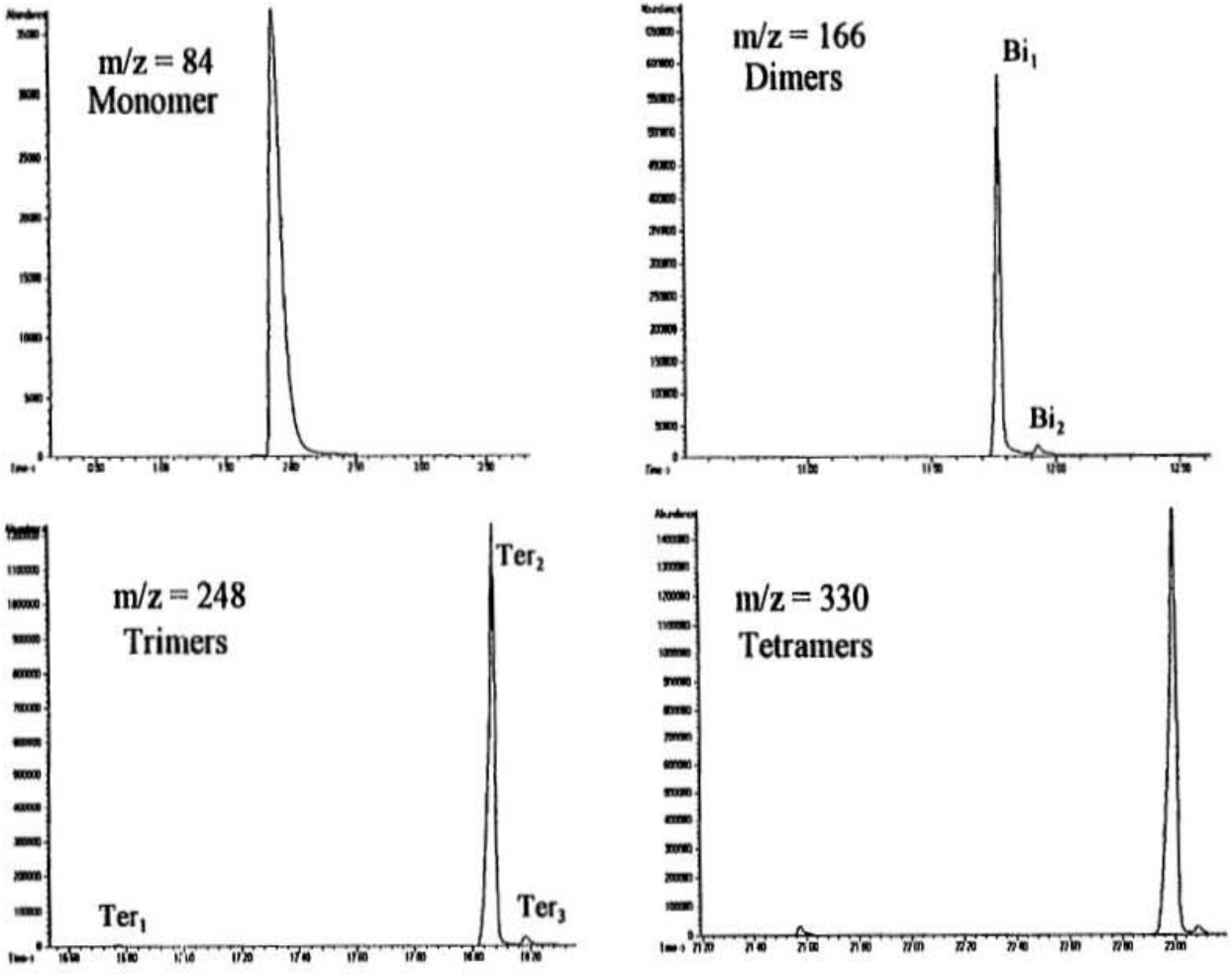


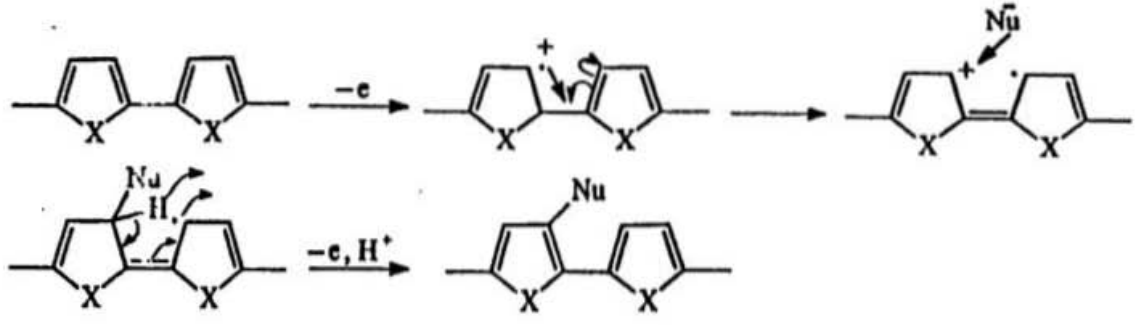
Figure 5.6 SIM pyrogram (T_{py} = 900 °C) of oligomers produced from pyrolysis of PTT. *Identities of the labeled peaks are shown in Figure 5.4.*

- synthesized conducting polymer under high potential by the reaction of the polymer with a nucleophilic reagent such as an OH group. Overoxidation of a conducting polymer causes, in most cases, damage to the polymer's conductivity and changes its electroactivity, especially when a higher voltage is required whether for synthesis, or, for p-doping (oxidation) of the polymer [14].

Compared to the potentials (used in electrochemical synthesis) for PBT (1.1 V) and PTT (0.9 V), a much higher potential of 1.6 V is required for PT when employing thiophene as the starting material. Overoxidation of PT is more likely to occur during its electrochemical synthesis and polymer deposition and is one of the major reason for poor quality in PT.

The basic mechanism for overoxidation of polythiophene and polypyrrole, shown in Figure 5.7, is widely accepted [14]. In solvents containing water (even traces of water), H_2O can attack electrophilic sites on the polymer backbone, leading to substitution forming carbonyl groups and possibly multiple substitution of some rings. Details of the reaction, including the extent of substitution and the formation of other functional groups, depend on the polymer and experimental conditions [14].

The study uses IR analysis to confirm the presence of oxidized groups in electrochemically-synthesized PT. Py-GC-MS is used as a complementary technique to



For Nu = OH

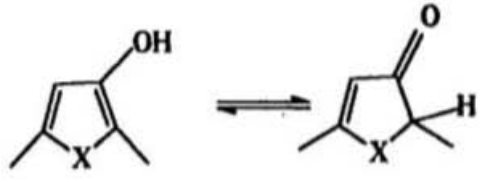


Figure 5.7 Overoxidation reaction mechanism for polythiophene and polypyrrole.

help identify the oxidized thiophene units.

5.2.2.1 IR Analysis

Figure 5.8 illustrates a comparison of the IR spectra of PBT, PT and overoxidized PT (addition of small amount of H_2O). The vibration absorption band at 1661cm^{-1} due to carbonyl groups appears in the IR spectrum of PT but not in that of PBT indicating that some of the thiophene was overoxidized. The intensity of the carbonyl adsorption band (1677cm^{-1}) in the spectrum of "overoxidized" PT (polymerized under the same conditions as that for PT but with the addition of 15 µl H_2O) is much greater. This supports the evidence of oxidation of PT and strongly suggests that more thiophene units in "overoxidized" PT were oxidized under these conditions. The carbonyl group shifting from 1661 to 1677 cm^{-1} indicates that the conjugation length in "overoxidized" PT is shorter than that in PT. Some researchers believe that overoxidation of PT can also result in the formation of the sulphone groups [38, 39]. Sulphone groups (1150 and 1300 cm^{-1}) are not evident in the IR spectra, but may be masked since they are in the same region as C-C stretching.

5.2.2.2 Pyrolytic Analysis

The polymers PT, "overoxidized" PT and PBT were subjected to pyrolytic analysis

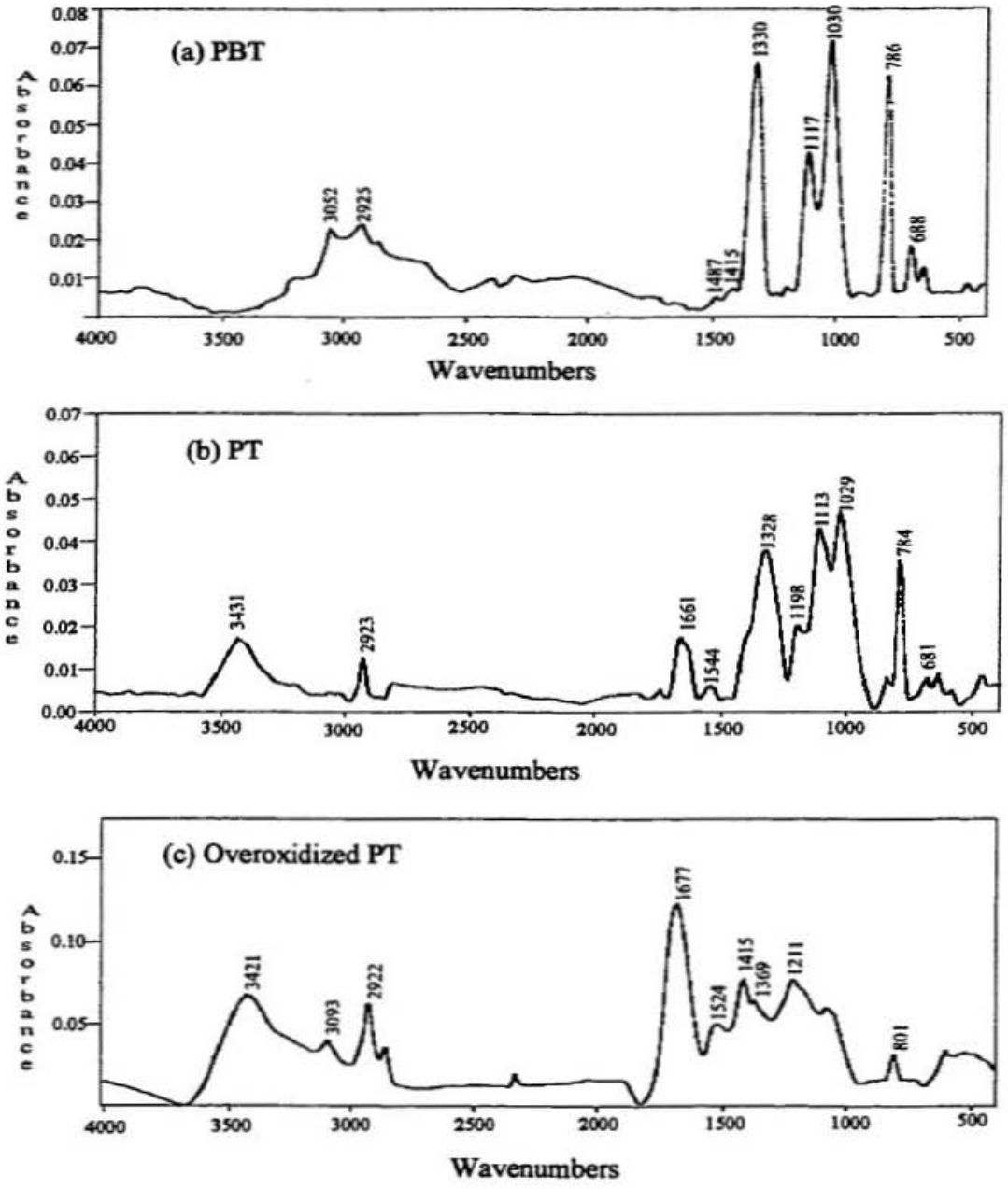
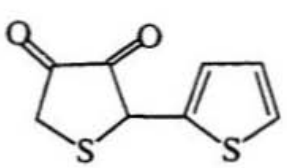


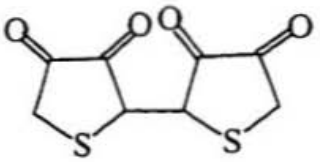
Figure 5.8 IR absorption spectra of (a) PBT (b) PT and (c) overoxidized PT.

at 300 °C and 900°C. One unique pyrolysate was observed from the PT polymers but not from PBT. From mass spectral data (Figure 5.10) the apparent molecular weight of the compound is 198 dalton. An additional product was observed from overoxidized PT with a molecular weight of m/z 230. The presence of these products is more clearly observed in the pyrogram at 300°C as shown in Figure 5.9 (The large peak in the pyrogram of PBT represents trapped bithiophene starting material). In these pyrograms (T_{py} = 300°C), the more strongly-bonded conjugated (unoxidized) polymer remains unpyrolyzed. There is a large increase in the abundance of product M.W. 198 in the "overoxidized" PT (Figure 5.9(c)) suggesting that this compound is responsible for the increased carbonyl adsorption band in the IR spectrum of "overoxidized" PT.

Tentative structures for these compounds are illustrated below and were deduced from interpretation of their mass spectra and an assumption that they contain carbonyl groups. There are no mass spectral reference data for these compounds. Their formation is reasonable based on proposed mechanisms described above.



M.W. = 198 (dalton) (**13**)



M.W. = 230 (dalton)

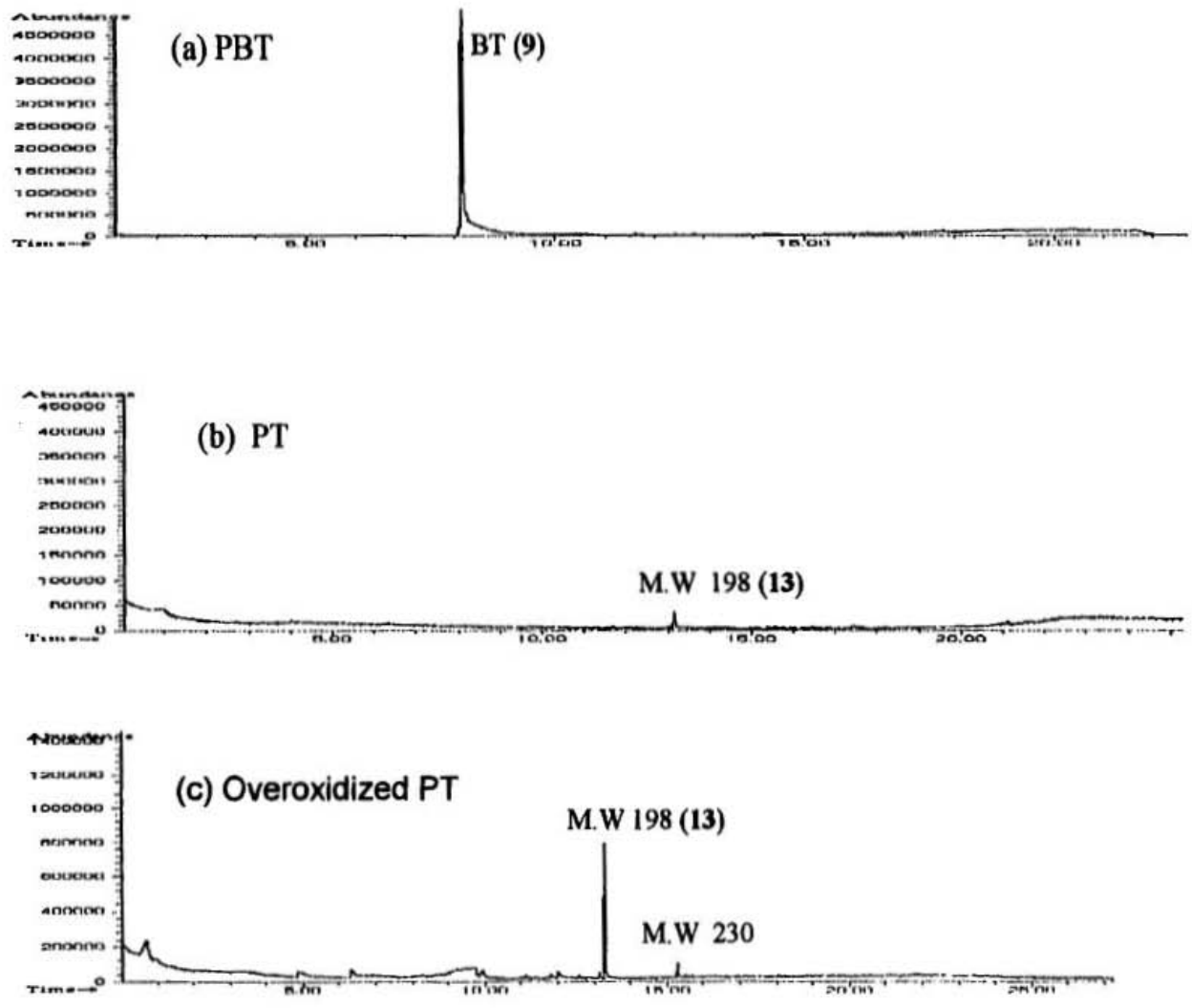


Figure 5.9 Pyrograms (T_{py} = 300°C) of (a) PBT (b) PT and (c) overoxidized PT.

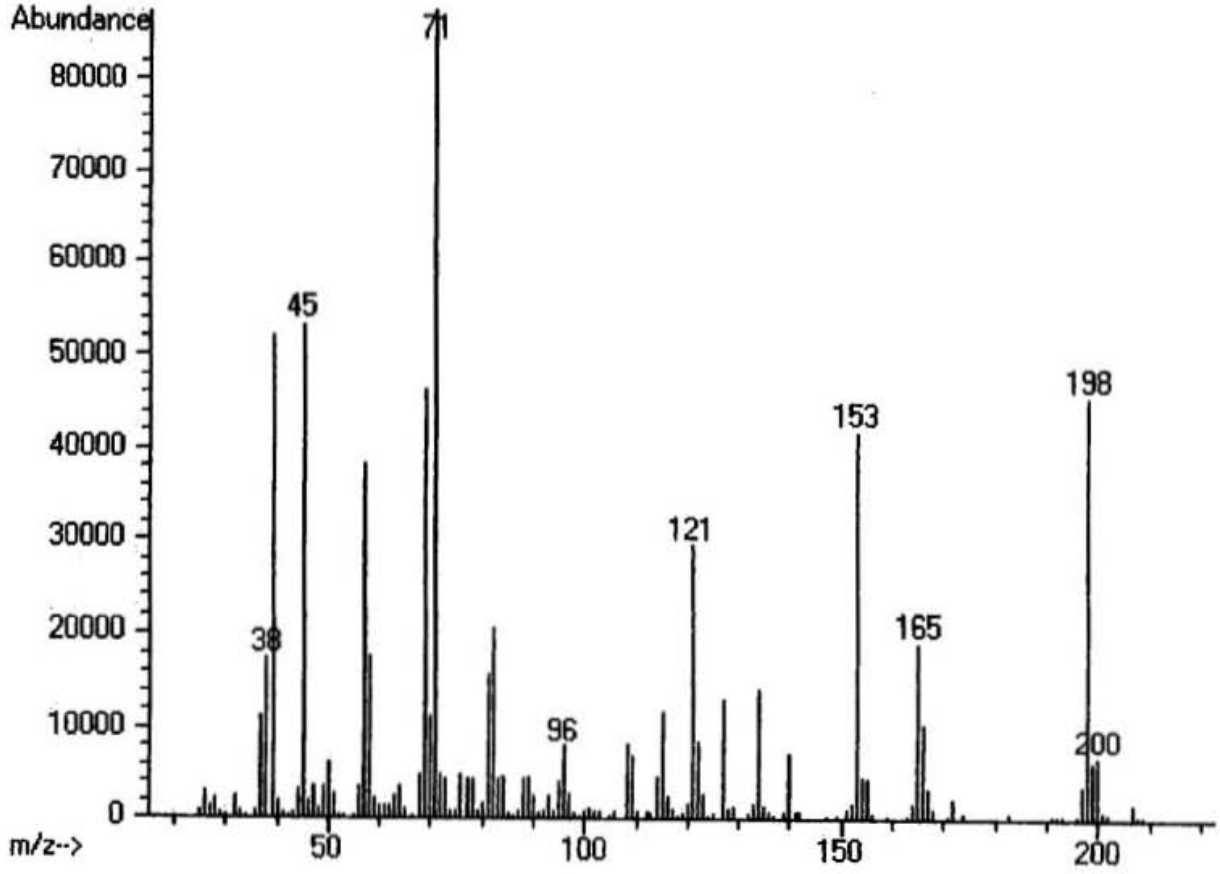


Figure 5.10 Mass spectrum of pyrolysis product (**13**).
Product with RT = 13.25 min as shown in figure 5.9.

5.3 Substituted Polythiophenes

5.3.1 Head (H) to Tail (T) Configurations

The planarity of a conjugated π system is another important factor that significantly affects the mean conjugation length of substituted polythiophenes. Introducing an alkyl group at the β -position of thiophene (e.g., 3-hexylthiophene) reduces the possibility of α-β' coupling between thiophene units and leads to a more stereoregular polymer. It has been reported that no α-β′ coupling was observed for a poly(3-alkythiophene) synthesized by the $FeCl_3$ method [22]. However, there are three relative orientations available when two 3-substituted thiophene rings are coupled between the α and α' positions, called head-tail (HT), head-head (HH), and tail-tail (TT), "diads". This can also lead to four configurational "triads" as shown in Figure 5.11. HH couplings cause a sterically driven twist of thiophene rings resulting in a loss of effective conjugation in the polymer. On the other hand, regioregular poly(3-substituted)thiophenes with a HT configuration can easily access a low energy planar conformation, leading to highly conjugated polymers. An increase of the torsion angles between thiophene rings lead to greater band gaps with consequent destruction of high conductivity and other desirable properties [22].

Figure 5.12 shows the SIM pyrogram of oligomers produced from poly(3-hexylthiophene) at 700 °C. One monomer, three dimers, and four trimers were identified. The three dimers and four trimers are isomers of each other based on their similar mass

spectra. The mass spectra for the three diads and four triads are shown in Figure 5.13 and Figure 5.14, respectively. Identification of these isomers could not be deduced solely from their mass spectra. They were positively identified by comparing their retention times with three diads and four triads reference standards kindly provided by Dr. Giovanna Barbarella (University of Bologna, Italy).

Figure 5.15 shows a pyrogram of poly(3-octylthiophene) (POT) pyrolyzed at 700°C. A similar series of three dimers was observed. One of the dimers at retention time 21.52 min was assigned the HT configuration, since this would be the major linkage configuration in the polymers. Trimeric products were not observed in the pyrogram of POT owing to their higher boiling points and the upper temperature limit of the GC analysis. The order of elution (HH<HT<TT) for the diads of POT is assumed to be the same as that observed for PHT.

Similar results were obtained from the analysis of poly(3-methyoxythiophene) (Figure 5.16).

From the above results it can be seen that the pyrolysis technique can supply structural information for the presence of multiple head, tail combinations existing in poly(3-substituted polythiophenes). This is very promising and, with suitable calculations it should be possible to calculate the regioregularity of poly(3-alkylthiophene) from their

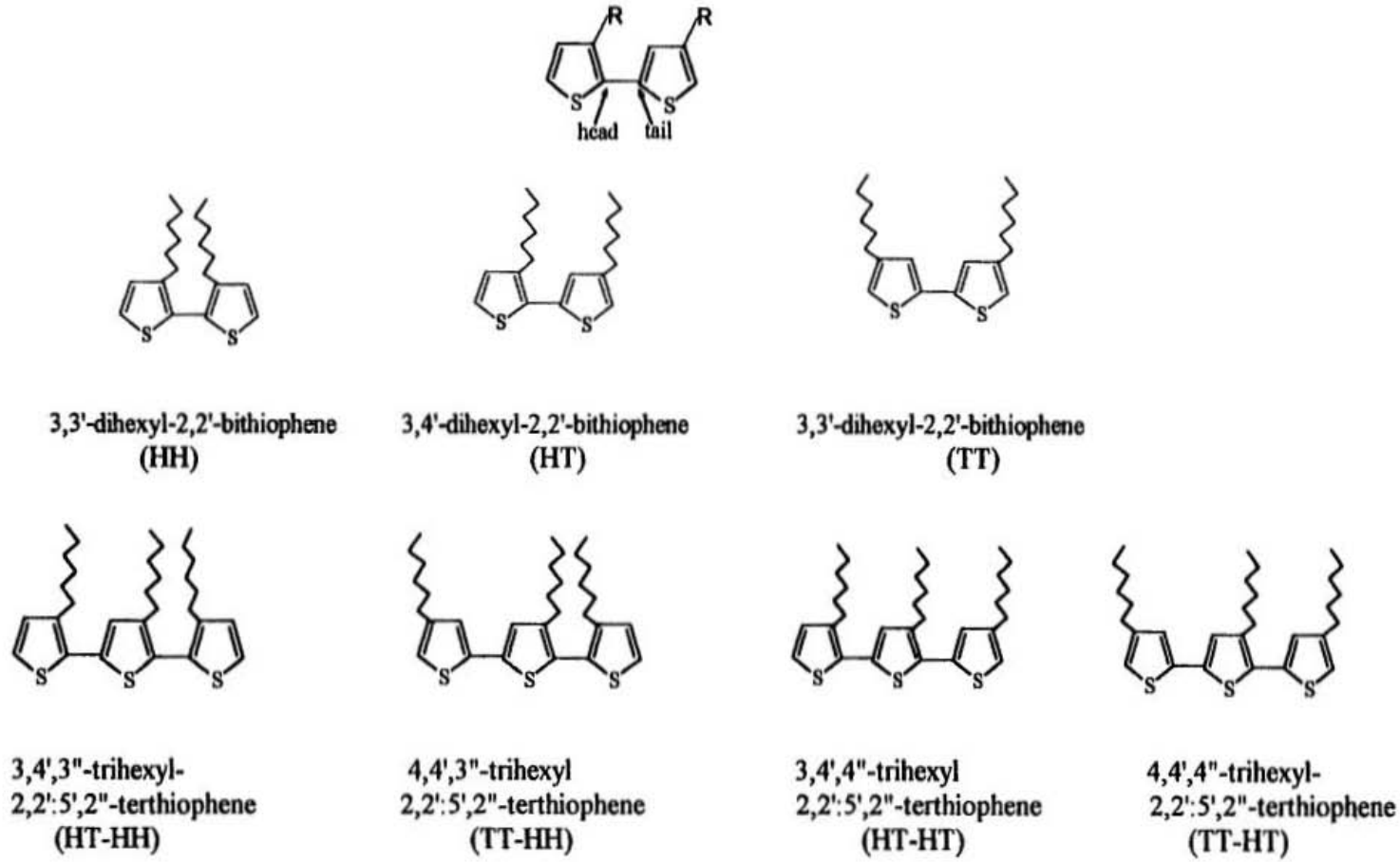


Figure 5.11 Possible configurations of diads and triads of PHT.

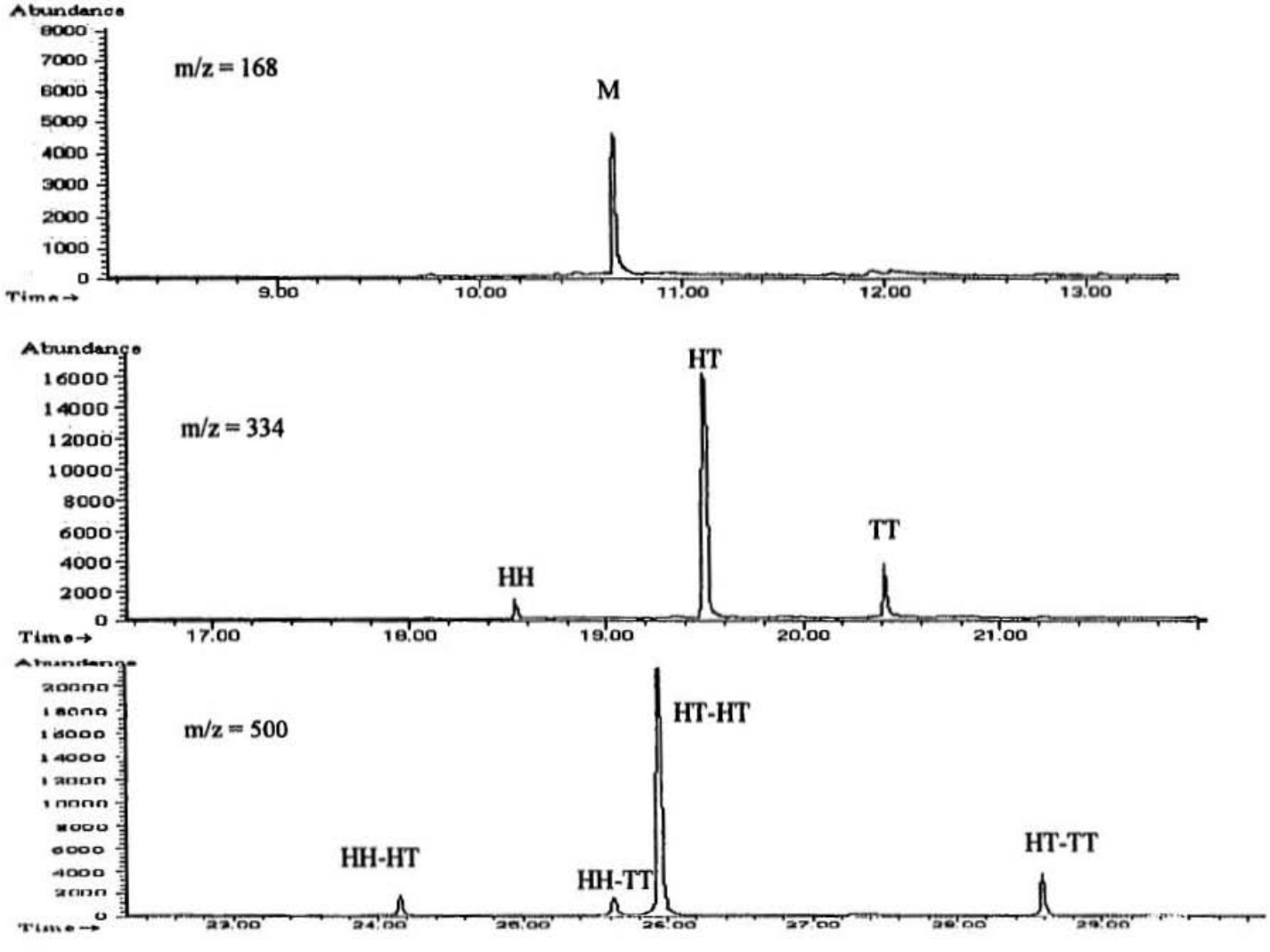


Figure 5.12 SIM pyrograms (T_{py} = 700°C) of oligomers produced from PHT.
The identities of the labelled peaks are shown in Figure 5.11

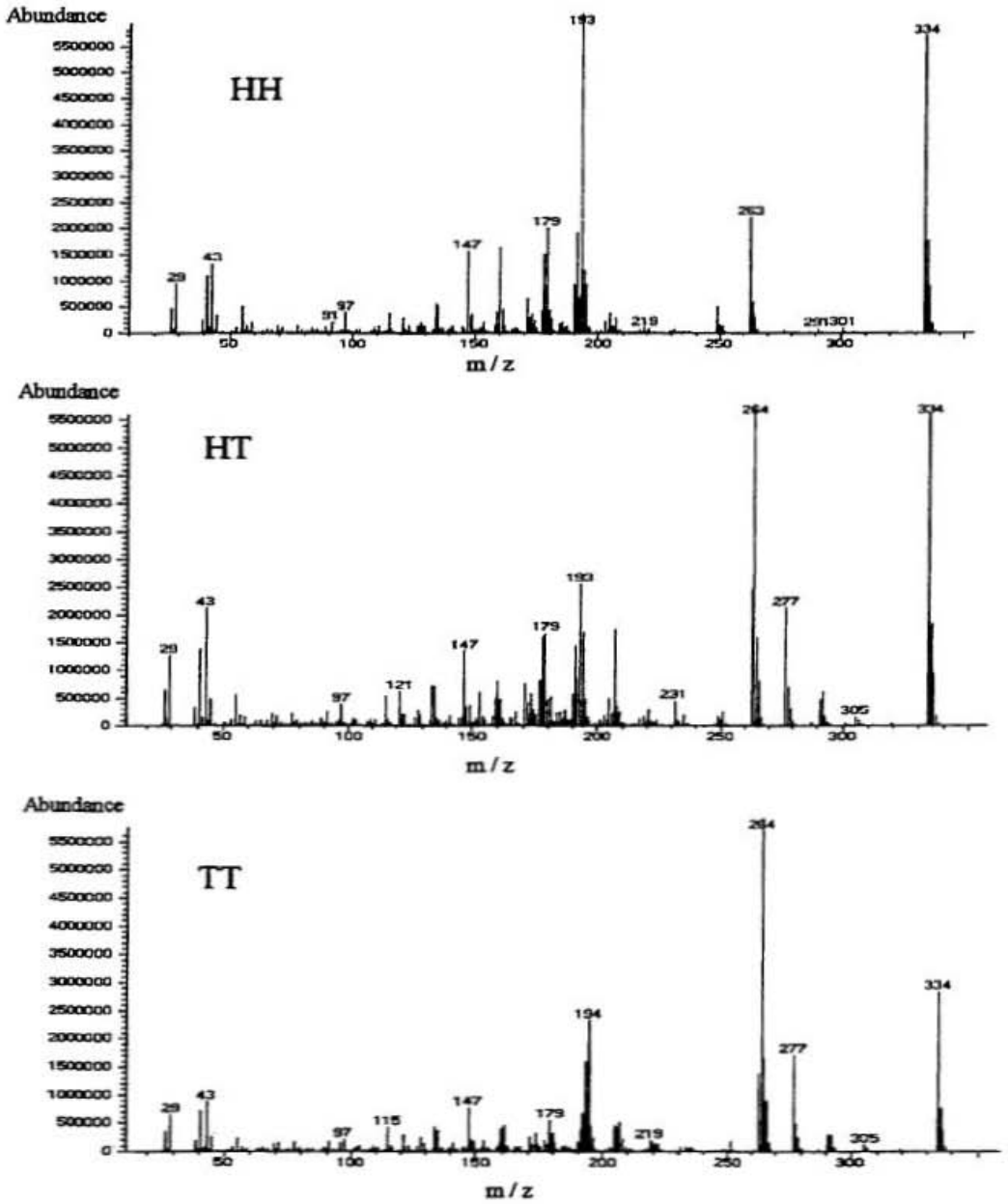


Figure 5.13 Mass spectra of the diads of PHT
Structures are shown in Figure 5.11.

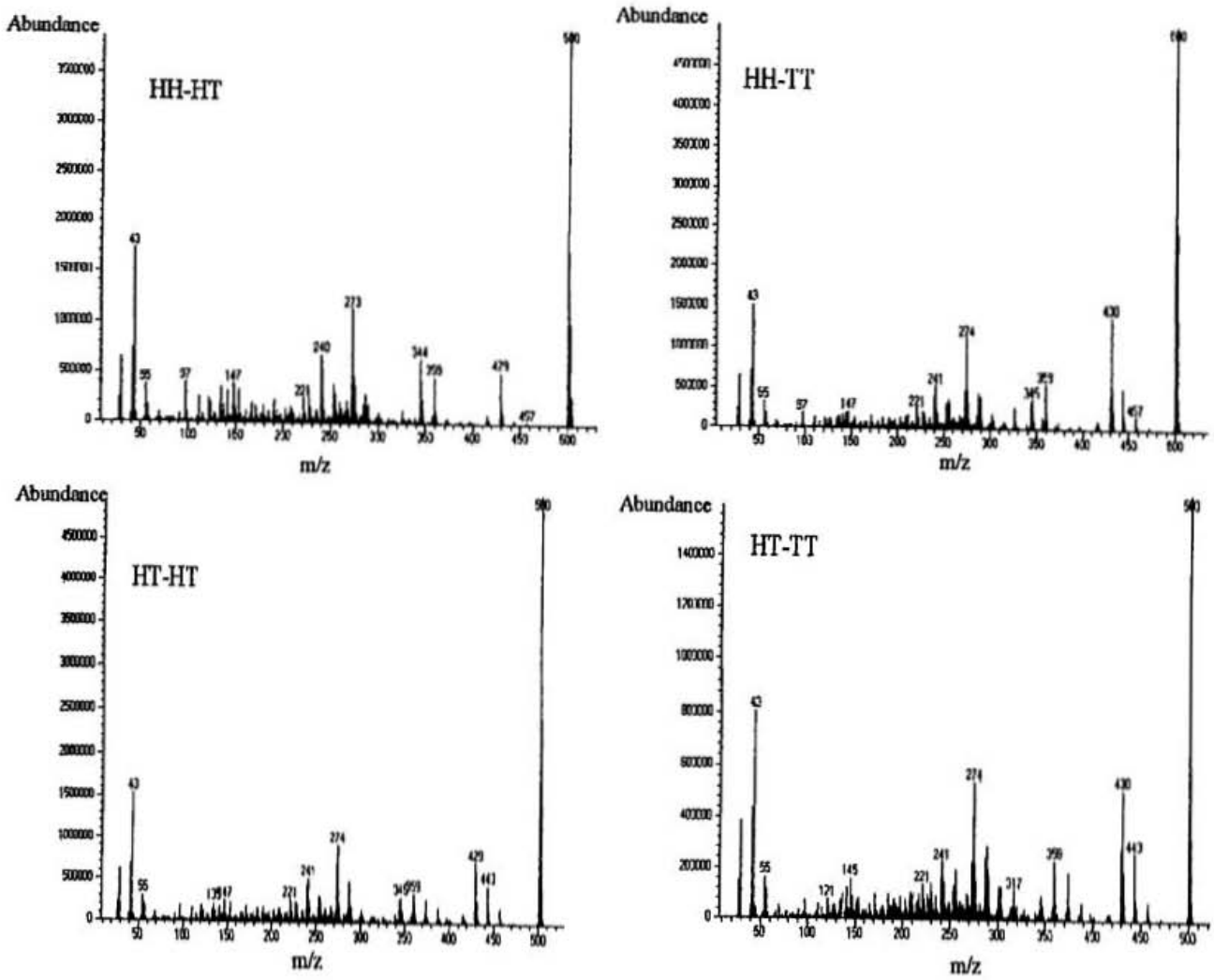


Figure 5.14 Mass spectra of the triads of PHT.
Structures are shown in Figure 5.11.

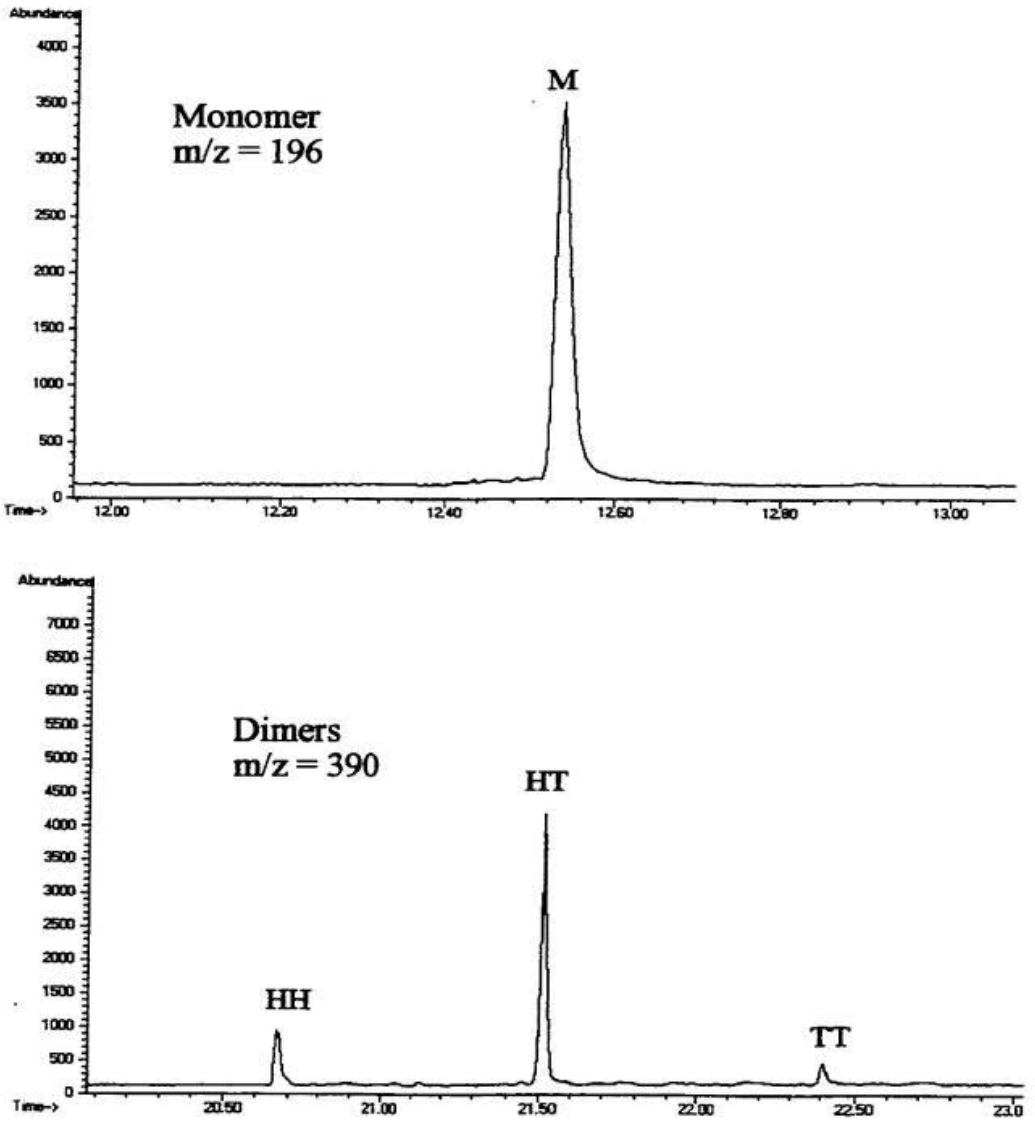


Figure 5.15 SIM pyrogram (T_{py} = 700°C) of oligomers produced from pyrolysis of POT.

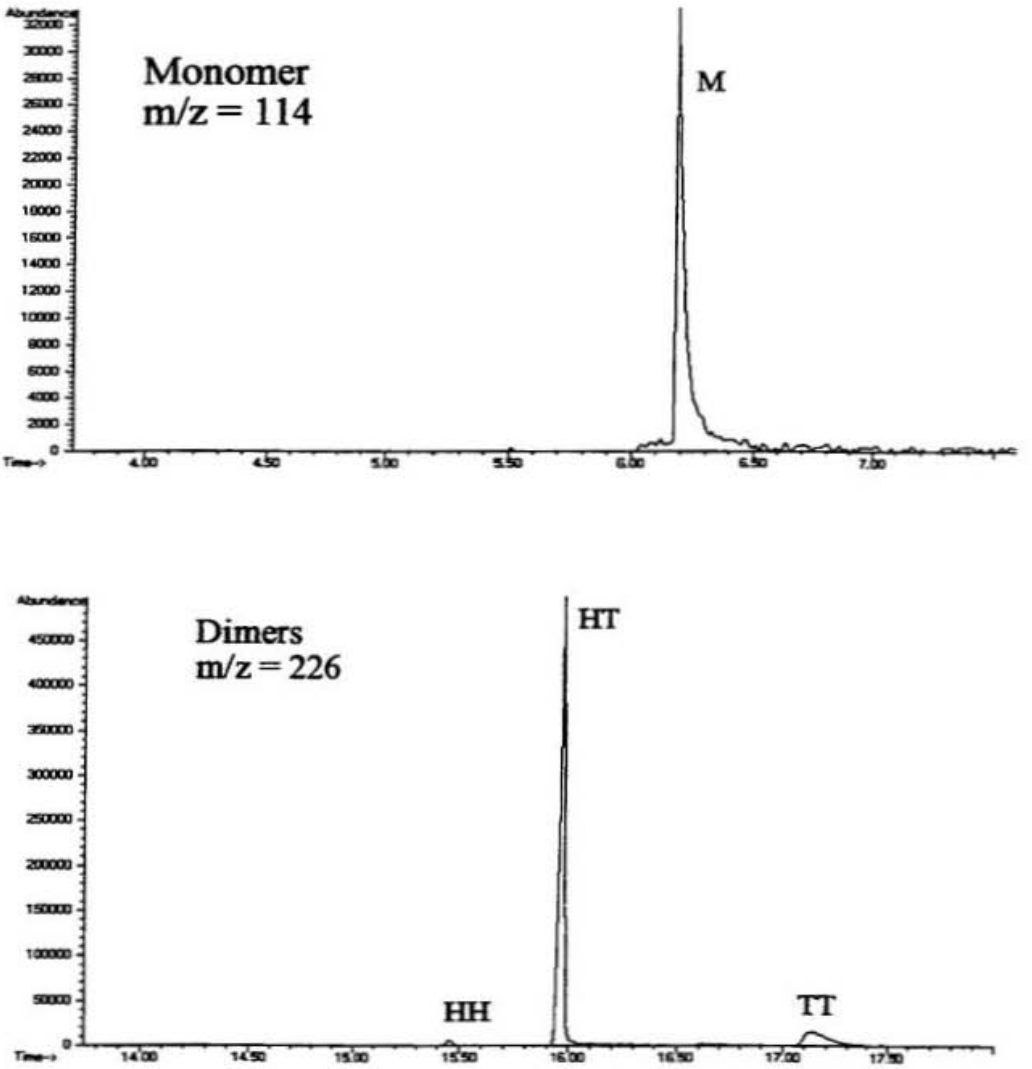


Figure 5.16 SIM pyrograms (T_{py} = 650°C) of oligomers produced from the pyrolysis of PMOT.

pyrograms.

5.3.2 Comparison of NMR and Pyrolysis Data

Normally, the regioregularity of 3-substituted polythiophenes is determined by proton NMR [55, 56]. The four singlet peaks in the aromatic region (6.98-7.06 ppm) of the spectra are attributed to the protons at the 4-position of the central thiophene ring in each configurational triad: HT-HT, TT-HT, HT-HH and TT-HH [18,42, 67]. Synthesis of these four isomeric trimers by Barbarella and his coworkers unambiguously assigned the relative chemical shift of each triad [68]. The chemical shifts are listed in Table 5.1. The regioregularity of poly(3-alkylthiophene) can be represented by the percentage of HT- HT as an integration of the HT-HT peak relative to that of the other non-HT-HT resonances.

Table 5.1 ^{1}H-NMR Chemical shifts corresponding to various configurational isomeres in PHT

Configuration*	Chemical shift (ppm)**
HT-HT	6.98
TT-HT	7.00
HT-HH	7.02
TT-HH	7.05

* as shown in Figure 5.11, ** from ref. 68.

Figure 5.17 shows ^{1}H-NMR spectra (300MHz) of poly(3-hexylthiophene) samples in the chemical shift range of 6.8 - 7.1 ppm. Two PHT samples were analyzed. One was bought from Aldrich and the other was synthesized by the $FeCl_3$ method. In the NMR spectrum of PHT (Aldrich), the large peak at 6.99 ppm is assigned to HT-HT. A "shoulder" peak exists in the spectrum. Its actual chemical shift is difficult to determine. The NMR spectrum of PHT (synthesized by $FeCl_3$) shows four peaks at chemical shifts of 7.06, 7.03, 7.01, and 6.99 ppm representing four configurational triads. Poor resolution however did not permit proper integration for regioregularity calculation. A higher magnetic field NMR instrument is necessary for quantitative analysis. Another problem with using NMR is the low solubility of the polymer in organic solvents.

The two PHT samples were also analyzed by pyrolysis GC-MS. Figure 5.19 shows the pyrograms of the Aldrich PHT and the chemically synthesized PHT. Much better quantitative data can be obtained compared to the results from proton NMR. In the chemically synthesized PHT, more HH and less TT configurations exist than those in the commercial PHT. Pyrolytic analysis shows that Aldrich PHT has more regular HT, consistent with the results of NMR analysis. Once a reasonable calculation method is formulated, the regioregularity of poly (3-substituted)thiophenes can be determined by this technique. This technique is quick and requires less sample and solubility of the polymer is not factor in its analysis.

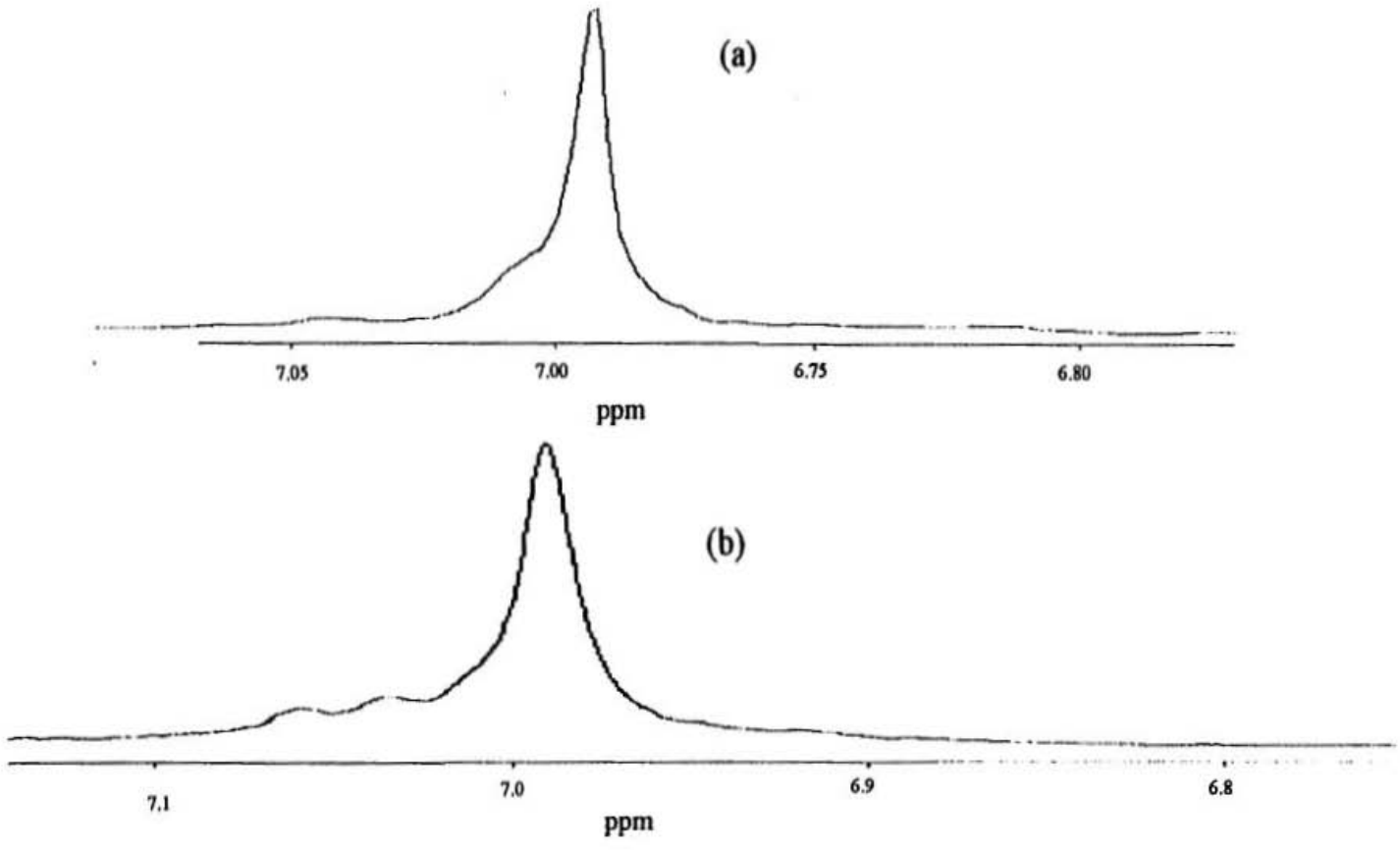


Figure 5.17 The expanded proton NMR spectra (300 MHz) of aromatic region for (a) Aldrich PHT and (b) chemically synthesized PHT

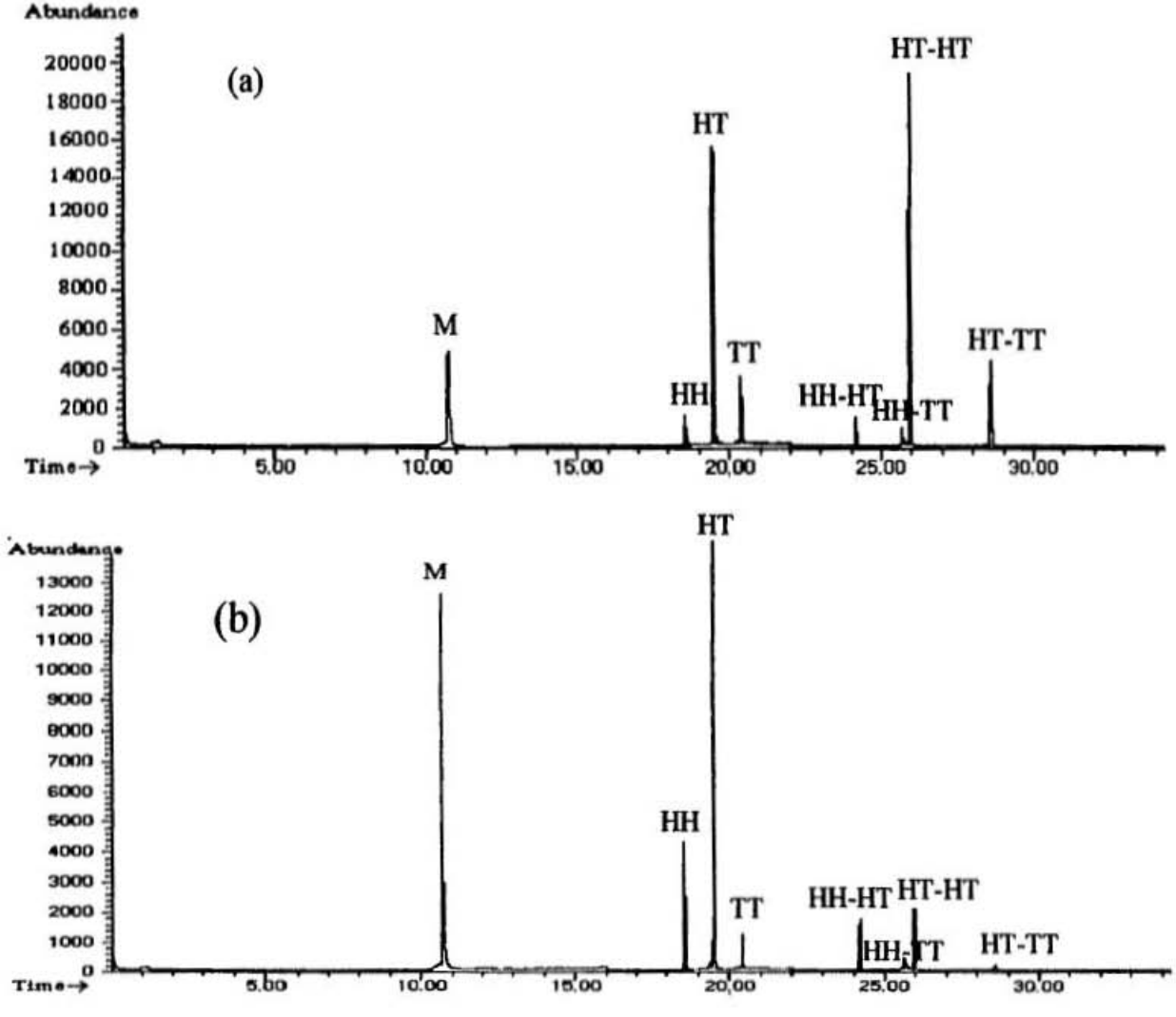


Figure 5.18 Comparison of SIM pyrograms (T_{py} = 700°C) from (a) Aldrich PHT and (b) chemically synthesized PHT.
The identities of the labeled peaks is given in Figure 5.11.

Chapter 6

Conclusion and Perspectives

In this study, Py-GC-MS has been demonstrated as a powerful technique for the analysis of the thermal behavior and microstructure of thiophene-based conducting polymers. Firstly, pyrolysis temperatures for high yields of structurally important fragments (e.g., monomer, dimers, and trimers) have been optimized for the conducting polymers employed in our study. A higher $T_{py.}$ 900°C, is required for the optimum pyrolysis of polythiophene (PT), polybithiophene (PBT), polyterthiophene (PTT), poly(3-methylthiophene) (PMT) and poly(3, 4-ethylenediox-thiophene) (PEDOT). A lower $T_{py.}$ (600 to 700°C) is required for poly(3-hexylthiophene) (PHT), poly(3-octylthiophene) (POT) and poly(3-methoxythiophene) (PMOT).

Secondly, a relationship between the conjugation length of unsubstituted polythiophenes (i.e., PT, PBT and PTT) and their pyrolytic behavior has been observed. The yield of H_2S gas produced from unsubstituted polythiophene decreases from PT (63%), PBT (36%) to PTT (13%) which reflects the decreasing conjugation length in the order of PT, PBT to PTT. In addition, the yield of high oligomer fragments increases from PT, PBT to PTT indicating that their polymeric qualities decreases from PT, PBT to PTT. This has

been confirmed by pyrolytic analysis of successively polymerized PT, PBT, and PTT (Section 4.5) and by IR analysis.

Thirdly, pyrolytic analysis of unsubstituted polythiophenes provides strong evidence that the predominant polymeric linkage is α-α′ linkage along with non-negligible amount of α-β′ linkage based on the presence of two isomeric dimers, three isomeric trimers and four isomeric tetramers appearing in the pyrograms of PT, PBT and PTT. The likelihood of α-β′ isomeric oligomers in the pyrogram has been further supported by the pyrolytic analysis of PEDOT. Only one dimer is observed in the pyrogram of PEDOT which is an exclusively α-α′ linked polymer. Evidence of partial overoxidation of polythiophene during its polymerization (due to its high oxidation potential, 1.6 V) can be obtained from the pyrograms, and is consistent with IR analysis results. Furthermore, structural analysis of oligomer fragments (i.e, three diads, four triads) obtained from pyrolysis of poly(3-alkylthiophene)s offers evidence that multiple head/tail structural configurations exist. By comparison of the pyrograms of commercial PHT and chemically synthesized PHT, it was shown that less HH configuration exists in commercial PHT than in chemically synthesized PHT. Further studies will be necessary to enable Py-GC-MS data to be used to calculate the regio-regularity of substituted polythiophene.

Finally, using fractionated pyrolysis, the study of the thermal degradation pathway of poly(3-alkylthiophene)s shows that the C_8 side chain of poly(3-octylthiophene) and C_6

side chain of poly(3-hexylthiophene) are cleaved at a lower temperature (e.g., 700°C than their thiophene-linked "back bones" which are cleaved at 900°C. It was also determined that the formation of H_2S is strongly influenced by the chemical environment of the thiophene ring.

This work has proven that analytical pyrolysis is a very useful technique for the characterization of thiophene-based conducting polymers. This technique is capable of providing both qualitative and quantitative structural information about the linkages of unsubstituted polythiophenes and the regioregularity of poly(3-alkylthiophene)s. However, further progress in the area (i e., polymer regioregularity) will require better understanding of the relationship between the regioregularity and the pyrolytic behavior of the polymer. Higher frequency NMR (or a solid state NMR) is required to obtain more quantitative information on polymer regioregularity for comparison with pyrolytic data.

An exciting area for future investigation is the study of conducting properties and "quality" of conducting polymers which can be investigated by analytical pyrolysis. Analytical pyrolysis has been used for quality control of the production of synthetic polymers. In the near future, the technique may be used for conducting polymers as well.

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